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The Deposition of Ice Crystals on Cooling Surfaces in Low Temperature Plant

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ABSTRACT. A study is made of the conditions governing the deposition of ice crystals from a moist air stream on to the inside surface of a cooled tube. The promoting effect of impurities such as oil vapour in the air stream is demonstrated. Series of experiments were made to establish the effect of air velocity, and of the temperature difference between the tube wall and air stream, on the amount of deposition. In the flow range tested (Reynolds' number 11,000 to 27,000) it was observed that increasing the air velocity increased the percentage deposition; at the lower velocities there was no evidence of progressive deposition. The effect of temperature difference on the percentage adhesion in the range 7° to 14° C. was small, but an experiment at a value of 4·6° C. showed a decrease in the amount of condensed snow deposited. In most experiments a glass tube was used but in others use of a brass tube gave similar results.

§ 1. INTRODUCTION

THE presence of small concentrations of condensable impurities, such as water vapour, in gases processed in a low temperature plant will lead to blockage of the plant unless some method of purification is adopted. The method of removal may use refrigeration or it may employ a process external to the low temperature part of the plant. Where external means of purification are employed, such as drying with alumina gel, the removal is usually incomplete and some further device must be used if frequent shut-downs are to be avoided.

The refrigeration methods of purification normally employ duplicate heat exchangers or regenerators. Whilst one of the exchangers or regenerators is in use, the other is allowed to thaw out, or the condensed impurity may be revaporized by passing a return stream of gas over it. In both types of cooling apparatus it is desirable that the condensed solid should immediately adhere to the cooling surface and not be carried forward to a colder zone of the plant where it is more difficult to remove. An exception to this practice is the process described by Kornemann and Yendall (1944) in which a heat exchanger is so designed that carbon dioxide condensing from air at temperatures below about −110° C. is maintained completely in suspension and is subsequently removed by scrubbing the gas with liquid air.

Little information is available concerning the processes by which crystalline precipitates are formed and adhere to the cooling surface under the conditions prevailing in low temperature plant, but it is often apparent that all the condensed solid does not adhere to the cooling surface and that a part is carried on in suspension in the gas stream. It was the purpose of these experiments to study the deposition process and to make a number of measurements of the percentage adhesion of ice crystals condensing from a moist air stream under various flow and temperature conditions.

§ 2. APPARATUS

The deposition of ice from a moist air stream was made to take place on the inner surface of a tube of approximately $\frac{1}{8}$ inch inside diameter and 12 inches long, the tube being cooled by circulating cold ethyl alcohol around it. The design of this experimental heat exchange tube is shown in Figure 1. In the majority of the experiments a glass tube was used, to permit visual inspection of the deposit, though a few trials were made with a brass tube. The tube was positioned at the centre of a vacuum jacketed sleeve by means of ebonite cones. The cold alcohol was brought into the upper brass header and flowed through slots in the ebonite cones into the annular space between the vacuum jacket and the experimental tube. The alcohol was drawn off continuously through the lower brass

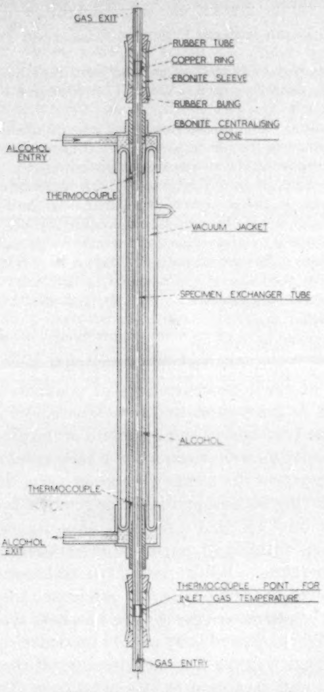
GAS EXIT
RUBBER TUBE
COPPER RING
EBONITE SLEEVE
RUBBER BUNG
EBONITE CENTRALISING CONE
ALCOHOL ENTRY
THERMOCOUPLE
VACUUM JACKET
SPECIMEN EXCHANGER TUBE
ALCOHOL
THERMOCOUPLE
ALCOHOL EXIT
THERMOCOUPLE POINT FOR INLET GAS TEMPERATURE
GAS ENTRY

Figure 1.

header. The temperature of the alcohol was measured by copper–constantan thermocouples inserted in the slots in the two ebonite cones.

In measuring the temperature of the air before entering and after leaving the experimental tube it was essential not to cause any obstruction of the gas path, or building up of snow might result. The method used was to insert into the air line, at either end of the experimental tube, a copper ring of the same diameter which was held in alignment by an ebonite sleeve. The copper ring achieved very closely the temperature of the air stream and its temperature could be measured by a thermocouple soldered to it.

The precooler and method of connection to the experimental heat exchange tube is shown in Figure 2. It is important that the condition of the air entering the specimen tube should resemble as closely as possible that prevailing at an intermediate point in a commercial exchanger. For this reason the precooling is carried out counter-currently, the final limb of the cooler being straight so that the 'carry-over' of ice crystals produced in the final stages of precooling would not be prevented. The precooler coil was of large diameter glass tubing to accommodate the ice deposited in experiments of long duration. The tube leading from the precooler to the exchanger was tapered gradually in two places and was provided with a 'Y' connection at the centre. The purpose of this connection was to provide a lead to the manometer and also to allow precooled air to be blown off whilst the temperatures were being stabilized.

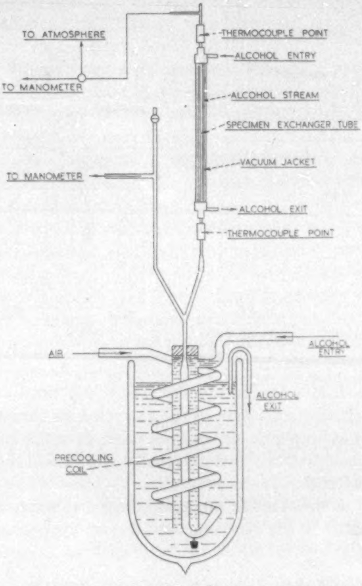
TO ATMOSPHERE
THERMOCOUPLE POINT
ALCOHOL ENTRY
TO MANOMETER
ALCOHOL STREAM
SPECIMEN EXCHANGER TUBE
VACUUM JACKET
TO MANOMETER
ALCOHOL EXIT
THERMOCOUPLE POINT
AIR
ALCOHOL ENTRY
ALCOHOL EXIT
PRECOOLING COIL

Figure 2.

§3. LAYOUT

The layout of the apparatus and design of the cryostat for maintaining temperatures down to −50° c. are shown in Figure 3. Separate alcohol streams were used to cool the precooler and exchanger, the temperature gradient between the two being adjusted either by varying the alcohol flow or by applying different currents to the electric heaters in each stream.

In order to continue the experiments for periods up to seven hours it was found necessary to reduce the humidity of the air entering the precooler. It was found more convenient to do this by continuously re-cycling the air and adding water vapour either by bubbling a fraction of the re-cycled air through water or more usually by admixing atmospheric air with re-cycled air at the compressor suction. The air leaving the compressor was water-cooled and passed through a glass-wool filter before being admittted to the precooler.

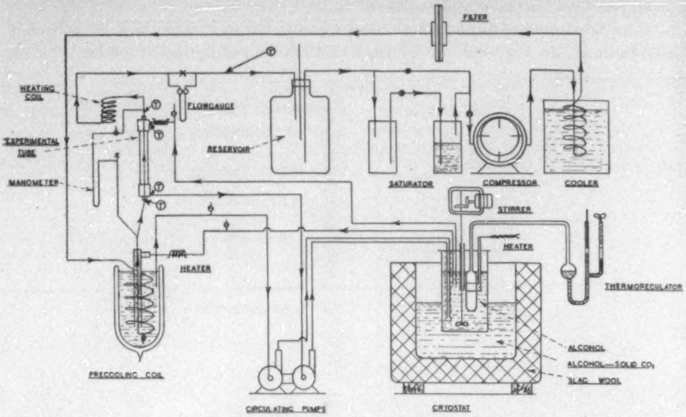
FILTER
HEATING COIL
FLOWGAUGE
EXPERIMENTAL TUBE
RESERVOIR
MANOMETER
SATURATOR
COMPRESSOR
COOLER
STIRRER
HEATER
HEATER
THERMOREGULATOR
ALCOHOL
ALCOHOL—SOLID CO_2
SLAG WOOL
PRECOOLING COIL
CIRCULATING PUMPS
CRYOSTAT
T

Figure 3.

The manometer connections to the experimental tube were so arranged that either the inlet pressure to the experimental tube, or the pressure drop across it, could be measured.

§4. EXPERIMENTAL OBSERVATIONS

The first experiment was made under the following conditions: air flow rate 1·4 ft^3/min., mean temperature of alcohol in exchanger −40° c., temperature of precooled air −34° c.

The temperatures of the precooler and tube were brought to the required value whilst the precooled air was being blown to waste, then the air stream was diverted to the tube. After about 10 minutes (the time taken for the connecting tube and insulation to cool down) the inside surface of the tube frosted over. This deposit was seen through a lens to be of uniform dendritic structure growing from points fairly evenly disposed over the tube surface. During the first 30 minutes the deposit was slightly denser towards the top of the tube, but this became progressively less apparent as the experiment proceeded. The particle size appeared to be of the order of 100 μ but it was impossible to see either the intricacies of the structure or the way in which the deposit was forming. After about 2 hours the deposition became less regular and narrow shelves of thicker deposit, lying at right angles to the direction of flow, were formed. The pressure drop across the tube increased from 10 cm. Hg to about 22 cm. Hg and the experiment was discontinued.

The apparatus was allowed to warm up and the condensates from the tube and the precooler were examined and were found to contain suspended oil droplets. The experiment was repeated and all the observations confirmed.

Since the air leaving the compressor was filtered through glass-wool the actual amount of oil depositing in the tube was small (less than 5% by weight), but it appeared possible that this oil was exerting a large influence on the deposition process. More efficient oil removal was therefore attempted by inserting a packed copper oxide tube, maintained at dull red heat, in the compressor delivery and filtering the effluent air, after cooling, through a paper filter. A repeat experiment showed that the rate of increase of pressure drop across the tube was reduced to approximately 20% of that experienced in the first experiment. Inspection of the condensate after thawing showed, however, that the oil removal was still incomplete, the length of the copper oxide tube probably being inadequate.

A third experiment was then made in which the rotor of the compressor was replaced by one adapted to take carbon blades. All parts of the compressor were cleaned with carbon tetrachloride and the compressor was thereafter run without oil. The third experiment again showed deposition starting after about 15 minutes, but subsequent deposition occurred very slowly and the structure of the deposit was finer than before. The increase in pressure drop in this case was only 4·0% of that occurring in the first experiment.

Even in the third experiment the condensate in the precooler was very slightly clouded but there was no sign of an oil film in the tube. From these results it is apparent that the presence of oil vapour exerts a very large influence on the deposition process.

§ 5. EFFECT OF AIR VELOCITY

Using the non-lubricated air compressor and the paper air filter a number of experiments were made for different air flow rates, the temperatures being maintained approximately constant. The experimental tube was carefully cleaned before each experiment by drawing through the tube a cotton-wool plug soaked in acetone.

The results of these experiments are shown in Figure 4. The slope of these curves indicates that increasing the gas velocity increases the amount of adhesion, but a more complete analysis of the results is necessary to establish the quantitative relationships. This is complicated by the fact that a change of flow rate not only causes a direct change of pressure drop across the tube but also changes the amount of water vapour admitted to the tube, the mean pressure of the system, and the exit air temperature.

The variable it is required to follow in any experiment is the proportion of the snow condensed which actually adheres to the tube wall. Although it is not possible to measure either of these quantities directly, it is possible to estimate them from the pressure, temperature and flow readings. If the effects of supersaturation are small the amount of snow being condensed is given by the product of the air flow rate and the difference in vapour pressure of ice at the inlet and outlet air temperature. The amount of snow adhering to the tube can be found indirectly by calculating the reduction of area of the tube by substituting the experimentally determined pressure drop in a formula for the flow of gases in tubes. In using such a formula, correction can automatically be made for small variations of mean pressure and temperature from one experiment to another. From the percentage reduction in area of the tube the thickness of the crystal layer or volume of the deposit can be found. From an assumed value of the bulk density of snow under these conditions the weight of snow adhering to the tube may be calculated.

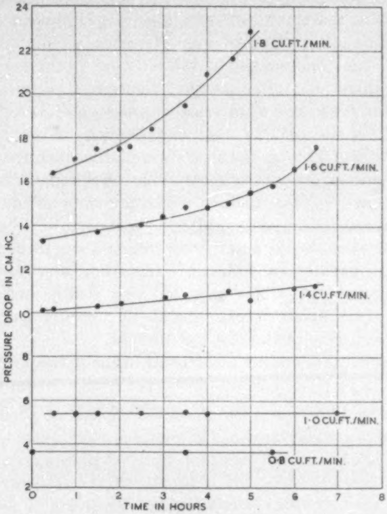

Figure 4.

The following formula for the flow of compressible fluids through pipes (McAdams 1942) was used:

$$\Delta p = \frac{G^2}{g_c}(v_2 - v_1) + \frac{2f_m G^2 L}{g_c \rho D}$$

where Δp = pressure drop across tube, G = mass flow per unit area, g_c = gravitational constant, v_1, v_2 = initial, final specific volumes, f_m = friction factor, L = length of tube, ρ = mean density of fluid, D = tube diameter ≡ 0·129 in. (0·01075 ft.).

In applying this formula it was found that the first term was always less than 1% of the total and could therefore be neglected. Hence

$$\Delta p = \frac{2f_m G^2 L}{g_c \rho D^5}.$$

If x is the total mass flow per unit time and C_1, C_2 are constants depending on the units employed, then

$$\Delta p = C_1 \frac{f_m x^2 L}{\rho D}.$$

For the range of Reynolds' numbers R from 5,000 to 200,000 Koo (1932) states that

$$f_m = \frac{0.046}{(R)^{0\cdot 2}} = \frac{0.046}{(4x/\pi D\mu)^{0\cdot 2}},$$

therefore by substitution,

$$\Delta p = C_1 \frac{x^2 L}{\rho D^5} \cdot \frac{0\cdot 046}{(4x/\pi D\mu)^{0\cdot 2}} = C_2 \frac{x^{1\cdot 8} L \mu^{0\cdot 2}}{D^{4\cdot 8}\rho}$$

or

$$D^{4\cdot 8} = C_2 \frac{x^{1\cdot 8} L^{0\cdot 2}}{\rho \Delta p}.$$

Both x and ρ can be determined from the experimental readings and the value of C_2 can be calculated. From a test experiment in which no deposition occurred the calculated value of D was 0·01072 ft., which compared closely with the measured value of 0·01075 ft.

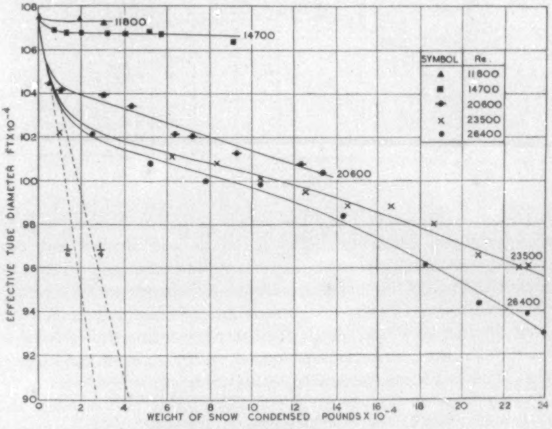

Figure 5.

In applying the above equation to the experimental results a further correction must be made for the uncooled parts of the tube, in which no deposition is assumed to occur.

Figure 5 shows the results for varying flow rates (expressed as Reynolds' number), plotted according to this revised method. The dotted curves show the decrease in diameter which would occur if all the condensed snow adhered to the tube wall, assuming a bulk density of snow of $\frac{1}{4}$ and $\frac{1}{6}$ respectively.

From this graph it appears that the initial rate of deposition was high but that it fell off rapidly to zero in the case of low gas velocities and to a value of approximately 10% at higher velocities. The first layer of ice crystals to deposit will present a roughened surface to the gas flow and therefore will produce a pressure effect out of proportion to the layer thickness. Therefore the initial slope of these curves may be somewhat steeper than is actually the case.

§6. EFFECT OF TEMPERATURE HEAD

A further series of experiments was made in which the air flow rate was maintained constant at 1·4 ft^3/min. and the inlet air temperature at approximately -31°c., whilst the temperature of the alcohol in the heat exchanger was varied from approximately -36° to -50°c.

The results of this series are shown in Figure 6, and with the revised system of representation in Figure 7. The temperatures shown in these diagrams are the mean temperature differences between the air and alcohol and represent closely the temperature differences between the air and tube wall. From Figure 7 it is apparent that the effect of temperature head in the range tested is small except in the case of the lowest value which gives evidence of zero adhesion. No exact comparison can be made of the slopes of the curves during the early part of the run because these are very largely influenced by the starting conditions of the experiment which could not be exactly reproduced.

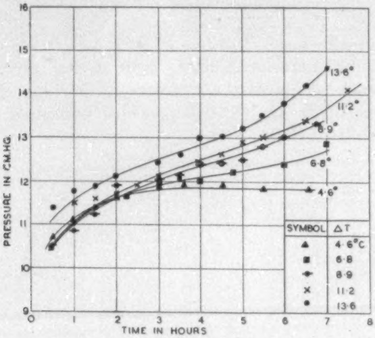

Figure 6.

§7. EXPERIMENTS USING A BRASS TUBE

A few experiments were made using a brass tube of 0·127 in. diameter in place of the glass tube previously used. The results of these experiments were very close to those for the glass tube formerly used, thus demonstrating that the material of the tube has little effect on the adhesion process.

§8. DISCUSSION OF RESULTS

In assessing the validity of these results the possibility of supersaturation of the air-stream must be considered. If the air flowing through the exchanger becomes supersaturated instead of precipitating solid the results of all the experiments would be misleading. This state of affairs is considered unlikely for the following reasons. The cooling surface of the precooler will rapidly become coated with ice crystals and further crystals will be held in suspension in the air stream, supplying abundant nuclei on which further condensation can occur. The connecting tube between the precooler and exchanger is short and heavily lagged so that the air entering the exchanger will still contain suspended crystals. In the exchanger the condensation will take place under similar conditions with a coating of ice crystals on the cooling surface and other nuclei present in the air stream. In the experimental tube supersaturation will be less likely, due to the higher degree of turbulence. The fact that the deposition of crystals was uniform over the whole length of the tube, except in the cooling down period when the air entering the exchanger was superheated, confirms the fact that the supersaturation is slight. If supersaturation were occurring to any great extent the deposit at the top of the tube would be much denser than the deposit at the bottom end.

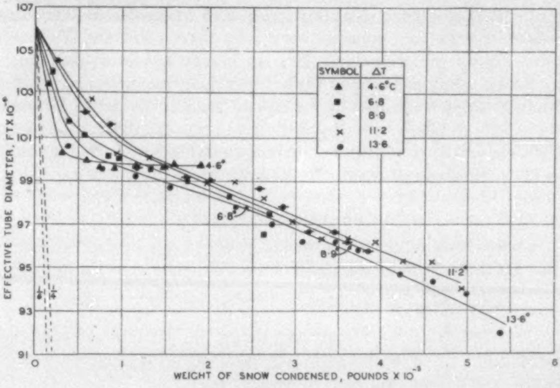

Figure 7.

In applying these results to an understanding of the processes occurring in low temperature plant it is at once apparent that unless a considerable quantity of oil is present in the entering gas it is very unlikely that all the precipitated solids will remain in contact with the cooling surface. In the case of regenerators of the conventional design the much lower gas velocity, combined with the tortuous gas path and the very small thickness of the deposit during each change-over period, may produce a greater amount of adhesion. In the case of tubular heat exchangers it seems possible that over a certain temperature and velocity range conditions may exist in which an exchanger could be run continuously without progressive deposition occurring and that the suspended solid could be removed at a later stage by filtration. Such a process is given added pertinence by the development of a successful filtering device (Hall and Haselden 1947) for ice crystal suspensions.

Any attempt to account theoretically for these results is made uncertain by the lack of information on the precise mechanism by which the production and growth of crystals takes place. Two mechanisms are possible: (i) All condensation takes place at the glass or metal interface and further growth of the crystals occurs chiefly whilst the crystals are in contact with the wall. When the crystals become too large they are partially or wholly eroded by the air stream. (ii) Condensation takes place by mixing of the cold boundary air layer with the turbulent main stream to produce small crystals suspended in the air stream. These crystals act as nuclei for further condensation which again occurs mostly at the interface between the boundary air flow and the main stream. Adhesion takes place, mainly due to thermal attraction of crystals to the cold surface.

For condensing liquids (Lewis 1927) substantial evidence is available to show that in the majority of cases process (i) is operative. In the given case, however, where the concentration of the condensable constituent in the gas phase is very small, and where the very open structure of the deposit has a large influence on the flow pattern of the air stream in the neighbourhood of the surface, it is likely that both processes are taking place. The relative importance of the two processes probably varies as the deposition proceeds, process (i) giving place to process (ii). It is also possible that migration of molecules over the surface of the deposited crystals can occur as shown by Estermann and Volmer (1927). Thus water vapour molecules may give up energy to the cooling surface and thereafter diffuse along the cooling surface and over the surface of the deposited crystals before taking a position in the crystal lattice. Evidence for mobility of molecules in ice crystals is given by Burton and Oliver (1935).

Further experiments, using ciné micrography, are now being undertaken to obtain more detailed information on the processes involved.

ACKNOWLEDGMENTS

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A Relationship between the Refractive Index and the Infra-Red Threshold of Sensitivity for Photoconductors

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ABSTRACT. It is shown that for photoconductive compounds the long wavelength 'threshold' of sensitivity λ should be related to the refractive index n of the photoconductor, and analysis of the available data shows that for the more highly refractive compounds n^4/λ always has a value close to 77. As a consequence of this relation, an explanation can be given for the change of the threshold wavelength with temperature which is observed for lead sulphide and similar materials. Suggestions are made as to what materials ought to be suitable for photoconductive detectors at longer wavelengths in the infra-red, and some confirmation of the ideas is shown by results obtained with cadmium arsenide, the properties of which are briefly described.

§ 1. INTRODUCTION

THERE are many materials now known for which the conductivity alters on exposure to radiation in the visible or near infra-red regions of the spectrum, but as yet there has been no explanation of the factors which determine the region of the spectrum to which a given material will be sensitive.

On the band theory of solids, insulators and semiconductors are materials for which the band of conduction levels is empty at the absolute zero of temperature and is separated from the filled band by a forbidden zone in which no levels exist for the pure material. Impurities or lattice imperfections, however, will give rise to levels in the forbidden zone.

The threshold of the photoconductive effect will occur at the wavelength where the quanta are just sufficient to raise electrons into the conduction band, or so near to the conduction band that thermal energies are sufficient to complete the process.

§ 2. THEORY

The general theory of photoconductivity worked out for F centres in alkali halides shows that absorption of the optical quantum first excites an electron without freeing it from the centre. The electron is then transferred to the conduction band by thermal energy from the lattice (Mott and Gurney 1940). It has often been suggested that even in so-called pure materials the photo-effect takes place only at preferred points in the lattice, such as vacant lattice sites, interstitial ions, or at atoms on the surface or in cracks, i.e. at any discontinuity in the lattice (Smekal 1929, Zwicky 1929, Gudden and Pohl 1926).

Any of these imperfections will create potential holes in the lattice capable of trapping electrons. An electron trapped at such a potential hole will be somewhat similar to an electron in an isolated atom, except that it is immersed in a medium of dielectric constant equal to that of the bulk material. Thus all the energy levels of the electron will be scaled down by a factor $1/(\kappa_{\text{eff}})^2$, where κ_{eff} is an 'effective' dielectric constant, which will approximate to the square of the refractive index (Mott and Gurney 1940). In principle the centre should have a line absorption spectrum, but in practice the lines are broadened into bands.

Hence the optical energy required to raise an electron at one of these irregularities into an excited state should be proportional to $1/\kappa_0^2$. We may thus expect that the threshold of the photoconductive effect, which is determined by the minimum energy required to raise an electron into an excited state, will vary inversely as the fourth power of the refractive index.

§ 3. EXPERIMENTAL DATA

Table 1 contains all the photoconductive compounds with refractive indices greater than about 2·5 for which both spectral sensitivity and refractive index data are available, with the exception of a few complex mixed crystals. According to Kurrelmeyer (1927) and Hughes and DuBridge (1932) the refractive index must be greater than 2 for photoconductivity to occur without artificially produced impurity centres.

§ 4. DISCUSSION

It will be seen that for the materials listed in Table 1 the values of n^4/λ are remarkably consistent. They all lie in the neighbourhood of 77 throughout a range of variation of n^4 from 35 to 230. For materials with refractive indices lying between 2 and 2·5 (mainly silver and thallium halides with barium, zinc and antimony oxides) the values of n^4/λ are somewhat lower and range from 72 for TlCl to between 47 and 58 for AgCl. Thus, although none of these materials gives results in complete disagreement with the relationship, it is clear that for lower values of the refractive index the variation of n^4/λ is considerable in view of the small range covered by n^4. It may be noted that for n greater than 2·25 values of n^4/λ are greater than 65, indicating that the relation becomes progressively worse as n decreases.

The fact that the values are so similar for such a wide range of compounds indicates that the photoelectrons are originating from the same type of lattice imperfection in all cases. Thus the centres cannot be formed from impurities, with the possible exception of oxygen, which may be present in any materials, even if manufactured with the most careful vacuum technique.

The most probable type of centre is an F centre, i.e. a missing negative ion replaced by an electron; or possibly an F′ centre if the potential hole has two bound electrons. According to Mott and Gurney (1940), the analogous centre consisting of a missing positive ion with a bound 'positive hole' (i.e. an electron missing from one of the adjacent negative ions) is also possible. These types of centre are just as likely to occur in any of the materials.

Pearson and Bardeen (1949) have recently carried out calculations on the excitation energies of boron impurities in silicon, assuming the energies to be sealed down by a factor κ^2, and obtained values in reasonable agreement with the thermally measured activation energies.

For photoconductive elements, which are not ionic crystals and where the photoconductivity is intrinsic, the relationship does not apply, and the values of n^4/λ vary widely.

It is concluded, therefore, that for the more refractive photoconductive compounds there is some theoretical basis and experimental evidence for an approximate relation between the 'threshold' wavelength and refractive index, namely $n^4/\lambda = 77$.

Table 1

Material	n	λ	n^4/λ	References	
				Refractive index	Wavelength
PbO	2·53, 2·66	0·53	85	Landolt–Bornstein	SIGESO 1945
HgS	2·58, 2·82 2·76, 3·06	0·63	84 113	Landolt–Bornstein *Int. Critical Tables*	Gudden and Pohl 1920
HgO	2·37, 2·5, 2·65	0·55	71	Landolt–Bornstein	Dechene 1939
$PbCrO_4$	2·5	0·55	71	Kapp 1935	Kapp 1935
Cu_2O	2·56	0·63	68	Landolt–Bornstein	Faltz 1937
Ag_2S	3·15 estimated	1·35	73	See note (*e*)	Coblentz and Kahler 1922
Sb_2S_3	2·9 approx.	0·8	88	Billings and Hyman 1947	Coblentz 1920
MoS_2	5·57, 2·33 3·3	2·0	84 59	Bailly 1938 Coblentz and Kahler 1919	Coblentz and Kahler 1919
CdS	2·43, 2·46	0·54	66	Landolt–Bornstein	Gudden and Pohl 1920
PbS	3·9	2·8	83	*Handbk. Chem. Phys.* 1948	Moss 1947
Tl_2S	2·9 estimated	1·0	71	See note (*e*)	Hughes and DuBridge 1932
	Average . .	. .	77		

Notes on the Table.

(*a*) It would be preferable to quote the refractive index in the region of the spectrum where the material is transparent and the dispersion small. However, few of the materials quoted have been measured over a large range of wavelengths, and so for consistency the index has been quoted for red light (0·65 to 0·75 μ) whenever possible. For most materials this wavelength should be in the non-absorbing region.

(*b*) For non-isotropic media with more than one refractive index the geometric mean has been used to calculate n^4/λ.

(*c*) Most of the measurements have been carried out on natural crystals, and both n and λ often vary from specimen to specimen, or as reported by different observers.

(*d*) In order to be applicable to the various types of spectral sensitivity curves which have been reported, the ‘ threshold ’ wavelength λ is taken as the point where the sensitivity finally begins to decrease rapidly. When the spectral curve is sharply peaked this wavelength is taken as the wavelength of maximum sensitivity. For materials where the sensitivity is roughly constant over a range of wavelengths, PbS for example, it is the point where the exponential drop begins on the long wavelength side.

(*e*) The refractive index of Ag_2S could not be found in the literature, but a fairly good estimate was obtained from data on reflectivity (Schneiderhohn 1931), using $R=(n-1)^2/(n+1)^2$, which gives a value of n equal to 3·4.

A second estimate was obtained from the refractive index of proustite, which is largely Ag_2S. It has the composition $3Ag_2S \, . \, As_2S_3$ and $n=2{\cdot}99$, 2·72, or a mean value of 2·85 (Landolt–Bornstein Tables). Since for As_2S_3 $n=2{\cdot}6$ (Landolt–Bornstein Tables), the refractive index of Ag_2S should be 2·9 approximately. The mean of these two estimates, namely 3·15, has been used.

Similarly, for Tl_2S, reflectivity data give $n=3{\cdot}0$ (von Hippel *et al.* 1946). Also, for $Tl_2S \, . \, As_2S_3$, $n=2{\cdot}72$ (Dana 1944). With $n=2{\cdot}6$ for As_2S_3, as above, we obtain for Tl_2S $n=2{\cdot}8$. Hence the mean value is $n=2{\cdot}9$.

(*f*) Schonwald (1932) has reported that for Cu_2O there is an additional band at longer wavelengths. It is of relatively low sensitivity and has not been included in the data of Table 1.

§ 5. TEMPERATURE VARIATION OF THRESHOLD WAVELENGTH

Since the threshold wavelength is determined mainly by the refractive index of the material, it is reasonable to suggest that the shift of the threshold to longer wavelengths on cooling, as observed for PbS, PbTe etc., is due to a temperature variation of the refractive index.

Unfortunately there seem to be no published data on the temperature variation of the refractive index for highly refractive materials. However, a rough estimate may be made in the following manner.

The Lorentz–Lorenz formula for the dielectric constant at optical frequencies is

$$\frac{\kappa_0 - 1}{\kappa_0 + 2} = CN\alpha,$$

where N is the number of molecules per unit volume, α the polarizability of the ions, and C a constant. Differentiating,

$$\frac{d\kappa_0}{dT} = \tfrac{1}{3}(\kappa_0 - 1)(\kappa_0 + 2)\frac{1}{N}\frac{dN}{dT}.$$

Now $\dfrac{1}{3N}\dfrac{dN}{dT} = \dfrac{-1}{3V}\dfrac{dV}{dT}$ = linear expansion coefficient for the material, $= -\beta$ say. Therefore $d\kappa_0/dT = -(\kappa_0^2 + \kappa_0 - 3)\beta = -\kappa_0^2\beta$ with sufficient accuracy. A similar calculation has been applied to the static dielectric constant by Bretsher (1934).

This relation shows that there will be an increase in κ_0, and hence in λ, with decreasing temperature. Up to the time of writing, the only materials measured which gave an increase of threshold wavelength on cooling are the PbS, PbSe, PbTe series, whereas for other materials on which data are available, i.e. Sb_2S_3 (Coblentz 1920) and ZnS (Moglich and Rompe 1942), there is a slight decrease of wavelength on cooling.

That any increase on cooling would be expected to be small for these latter materials follows from the fact that a large value of $d\kappa_0/dT$ necessitates both high refractive index and high expansion coefficient.

These conditions are fulfilled for PbS, for which $\kappa_0 = (3{\cdot}9)^2$ and $\beta = 20 \times 10^{-6}$ (*International Critical Tables*). Hence $d\kappa_0/dT = -46 \times 10^{-4}$. For Sb_2S_3, however, although the refractive index is high, 2·9, β is small, namely $1{\cdot}5 \times 10^{-6}$. Therefore $d\kappa_0/dT = -1{\cdot}1 \times 10^{-4}$. For ZnS the variation of the photoconductive threshold with temperature has not been measured. However, it would be expected to behave similarly to CdS, which shows a slight decrease of λ on cooling, especially as the long-wave edge of the absorption band decreases slightly in wavelength (from $0{\cdot}335\,\mu$ to $0{\cdot}325\,\mu$) in a manner similar to that observed in CdS (Moglich and Rompe 1942).

For ZnS, $\kappa_0 = (2{\cdot}36)^2$ and $\beta = 6{\cdot}7 \times 10^{-6}$, hence $d\kappa_0/dT = 2{\cdot}3 \times 10^{-4}$.

It is thus clear that while the effect of changing dielectric constant may be predominant in determining the temperature variation of λ for PbS, it will contribute little in the cases of Sb_2S_3 and ZnS.

The fact that there is a small change in the opposite direction for these latter materials is presumably due to some secondary process operating in the reverse direction, which becomes predominant when the dielectric change is sufficiently small. Such a process has been considered by Radowsky (1948), who has shown that there is a broadening of the electron energy levels due to interaction with the vibrating lattice. Thus increasing temperature broadens both the full and conduction bands of levels, and hence reduces the width of the forbidden zone. It is shown that the effect gives approximately the correct shift of the absorption edge in ZnS.

The magnitude of the wavelength change expected may be evaluated for PbS. For the temperature interval 290° to 90° K.,

$$\Delta\kappa_0 = \kappa_0{}^2\beta\Delta T = 0{\cdot}92.$$

Therefore
$$\frac{\lambda_{90}}{\lambda_{290}} = \left\{\frac{\kappa_0 + \Delta\kappa_0}{\kappa_0}\right\}^2 = 1{\cdot}13,$$

corresponding to a change from 3·0 to 3·4 μ. Although this is smaller than the observed values, it shows that the theory predicts for PbS a large increase of wavelength on cooling, in contrast to the small values of the wavelength changes when of the opposite sign. The limiting values observed by the author for PbS are: minimum 2·8 μ to 3·4 μ, maximum 2·9 μ to 3·8 μ.

The Lorentz–Lorenz formula is only an approximation, particularly for highly refractive materials, and a better check on the theory may be made by comparing the results for PbS and PbTe, so that any deficiencies in the above formula tend to be the same for both materials.

If E is the quantum energy corresponding to the threshold wavelength λ, then $E\kappa_0{}^2 = \text{constant}$. so that

$$\kappa_0{}^2\frac{dE}{dT} = \frac{-2\kappa_0 E\,d\kappa_0}{dT} = 2E\,d\kappa_0{}^3\beta.$$

Hence $(dE/dT)E^{-\frac{1}{2}}\beta^{-1} = \text{constant}$.

Values of this expression for PbS and PbTe are shown in Table 2. The agreement is seen to be satisfactory.

Table 2

	λ_{290}	Shift $\lambda_{90}-\lambda_{290}$	$\beta\times 10^{-6}$	$\frac{dE}{dT}E^{-\frac{1}{2}}\beta^{-1}$
PbS	2·8	0·6	20	30
	2·9	0·9	20	38
PbTe	3·5*	1·5	27	33

* Moss (1948) extrapolated to room temperature.

Note: All the threshold wavelengths are taken at the point where the sensitivity has fallen to 50%. The value of β for PbTe was measured by the author.

§ 6. DESIGN OF PHOTOCONDUCTORS FOR LONGER WAVELENGTHS

The relation found between wavelength of the photoconductive effect and the refractive index gives an indication of where to search for materials which will be photoconductive at longer wavelengths.

It is now possible to make PbS and PbTe detectors whose performance is more than a hundred times better than conventional infra-red detectors (such as thermopiles and bolometers), for comparable conditions of operation (Watts 1949, Simpson *et al.* 1948). This means that these photoconductors are superior to any other infra-red detectors within their spectral range, and it is thus of importance to extend this range to longer wavelengths. To this end the foregoing relation should be of value in shortening the tedious process of producing photoconductivity by trial and error in the many possible compounds so far uninvestigated.

It may be objected that there are no published data on materials of refractive index greater than that of PbS, and that it is not easy to measure such high refractive indices. However, if the above ideas are correct, considerable guidance as to where to search in the periodic table for new materials can be obtained by considering data on the polarizability of the ions. The higher the polarizability (with other things equal) the greater will be the refractive index, and consequently the wavelength for which the material may be photoconductive. The data on some of the comparable groups of photoconductors are given in Table 3. They are arranged in general so that the 'threshold' wavelength increases diagonally towards the lower right-hand corner. The polarizability of each ion is quoted beside the name of the ion, and the wavelengths (in microns) for various combinations of the ions given. Pauling's (1927 b) figures are used for the polarizability of the ions, except for Tl^+ from Wulff and Schaller (1934), and Pb^{++} from Wulff and King (1934).

Table 3

		Cl^-	Br^-	I^-	O^{--}	S^{--}	Se^{--}	Te^{--}
	$(\times 10^{-24})$	3·6	4·8	7·1	3·9	10	10·5	14
Zn^{++}	0·3				0·31 $\mu^{(1)}$	0·4 $\mu^{(2)}$		
Cd^{++}	1·1					0·54 μ	0·7 $\mu^{(3)}$	0·8 $\mu^{(3)}$
Hg^{++}	1·26			0·55 $\mu^{(4)}$	0·55 μ	0·63 μ		
Sb^{+++}					0·32 $\mu^{(8)}$	0·8 μ		
Bi^{+++}						1·0 $\mu^{(5)}$	1·1 $\mu^{(6)}$	1·6 μ or 2·8 $\mu^{(7)}$
Tl^+	3·7	0·36 $\mu^{(9)}$	0·41 $\mu^{(9)}$	0·45 $\mu^{(9)}$		1·0 μ		
Ag^+	1·7	0·38 $\mu^{(10)}$	0·43 $\mu^{(10)}$	0·42 $\mu^{(10)}$		1·35 μ		
Pb^{++}	3·7			0·52 $\mu^{(9)}$	0·53 μ	2·8 μ	3·6 $\mu^{(11)}$	3·6 $\mu^{(11)}$

References in Table: (1) Veselovski 1948; (2) Gudden and Pohl 1920; (3) Frerichs 1947; (4) Volmer 1917; (5) Coblentz and Kahler 1919, Asai 1940; (6) SIGESO 1945; (7) Measured by author; (8) Heintz 1923; (9) Coblentz and Eckford 1923; (10) Kirillow 1929; (11) Moss (1949 b), room temperature values.

The polarizabilities of the Sb^{+++} and Bi^{+++} ions are not known, but qualitatively the polarizability increases with atomic weight, so that Bi^{+++} will be the greater.

The wavelengths for the oxides and iodides are very similar, although the I^- ion has considerably greater polarizability. This is due to the fact that the I^- ion is large (radius 2·2 A. compared with only 1·3 A. for the O^{--} ion), with consequent reduction in the polarizability per unit volume. The I^- ion is almost identical in size with the Te^{--} ion, and hence a direct comparison can be made for these two.

It will be seen that the longest wavelength 'threshold' so far obtained is that for PbTe.

The superiority of the Pb^{++} ion may be appreciated from the fact that it has the largest polarizability quoted in the literature, and has also a relatively small radius (1·2 A.) compared with Tl^+ (1·44 A.) for example. Furthermore, the ion is divalent, and hence in the case of the telluride a larger fraction of the lattice space is filled by the more highly polarizable Te^{--} ion, compared with Tl_2Te, which increases the polarizability per unit volume.

Among the ions listed (or similar ones in the periodic table) the Te^{--} ion is clearly the most suitable negative ion, and it is doubtful if a positive ion superior to the Pb^{++} ion can be found. The most hopeful materials to try would seem to be Ag_2Te, Tl_2Te and Au_2Te, though it is almost certain that all three would be somewhat inferior to PbTe. The Au^+ ion has a polarizability $1 \cdot 9 \times 10^{-24}$ and radius 1·37 A. (Goldschmidt 1927, Pauling 1927a, for ionic radii).

The metals in the first four columns of the periodic table with their normal valencies (i.e. Li^+, Be^{++}, B^{+++}, C^{++++} and their congeners) do not seem very promising. No figures are available for the molybdenum–tungsten series, which might be worthy of investigation. Further work should also be done on bismuth compounds, since Bi_2S_3 has been described as possessing some sensitivity out to $7 \cdot 0\,\mu$ (United States Patent Specification 1941). What seems a much more fruitful field for research is the investigation of the completely untried series of compounds with trivalent negative ions. Table 3 shows that for ions of the same size (e.g. I^- and Te^{--}) the divalent ion has much higher polarizability and results in much longer wavelengths. For comparison, the As^{---} ion, which is the same size as the I^- and Te^{--} ions, has the very high polarizability of 28×10^{-24}. If, therefore, photoconductive layers of arsenides could be prepared, a definite increase in the wavelength range would be expected.

Photosensitive layers of one such material have now been prepared, viz. cadmium arsenide, Cd_3As_2. The spectral sensitivity curve has been measured, and the 'threshold' wavelength is found to be beyond 2·0 microns. This is a very large increase over the wavelength of $0 \cdot 8\,\mu$ for CdTe, particularly compared with the small increase resulting on going from CdS to CdTe. The properties of this material are described in the Appendix.

This result is adequate confirmation of the idea that the arsenides as a class should be sensitive to longer wavelengths. If sensitive layers of lead arsenide (and possibly silver or thallium) can be made, there is every hope that they will extend the present range of photoconductive detectors further into the infra-red region.

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APPENDIX

PROPERTIES OF CADMIUM ARSENIDE

The arsenides represent a class of semiconductors and photoconductors which have not as yet been investigated.

(i) *Preparation.*

The compound Cd_3As_2 was prepared by direct fusion of the elements. The materials were weighed out with a slight excess of arsenic and inserted into a Pyrex tube. The tube and contents were outgassed *in vacuo* at 160° c. and then sealed off from the system (pressure 10^{-6} mm. Hg approx.). The tube was baked at 610° c. for two hours. A few milligrams of the resulting material were used in the manufacture of a typical layer, the method of preparation being similar to that previously used for tellurium layers (Moss 1949 a).

(ii) *Resistance.*

The resistance of one layer was measured over the temperature range 90° to 390° K. The results are plotted as log (resistance) against reciprocal temperature in Figure 1. The curve is roughly linear between 390° and 180° K., and corresponds to $R=R_0 \exp(\epsilon/2\boldsymbol{k}T)$, where $\epsilon=0{\cdot}14$ ev. Presumably the slope of the line would be steeper if the material could be made more accurately stoichiometric, in a similar manner to PbS (Hinterberger 1942). The resistance was substantially constant below 140° K.

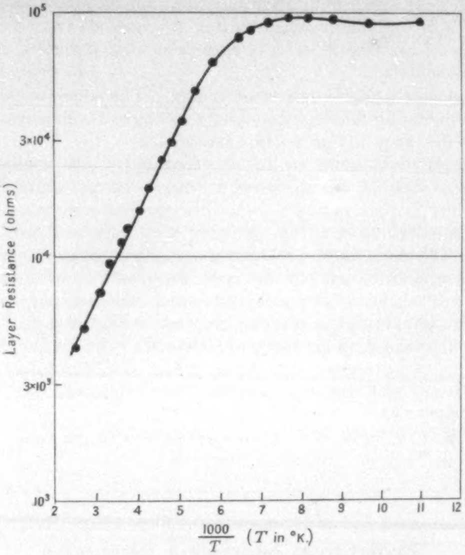

Figure 1. Resistance temperature relation for Cd_3As_2.

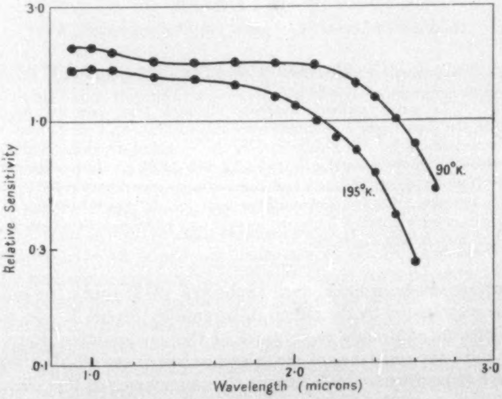

Figure 2. Spectral sensitivity curves for Cd_3As_2.

At room temperature the resistance was 10^4 ohms (the layer dimensions being 1 mm. gap between 3 mm. electrodes and approximately 10^{-3} mm. thick), which corresponds to a specific resistance of 3 ohm cm.

(iii) *Type of current carriers.*

For all samples thermo-electric power measurements indicated that the carriers were electrons.

(iv) *Photoconductivity.*

The layers were sensitive only when cooled. The response times, measured as the time required for the electrical signal to decay to $1/e$ on removal of the light signal, lay in the range 10^{-3} to 4×10^{-3} second.

The spectral distribution of the photosensitivity was measured, using a monochromator with a lithium fluoride prism. The A.C. signal from the layer produced by the chopped radiation from the monochromator was passed through a high gain amplifier tuned to the chopping frequency and read on a rectifier type meter. The signal output, referred to a constant energy spectrum, is plotted against wavelength in Figure 2 for two layer temperatures, 90° and 195° K.

It will be noted that the wavelength at which the sensitivity starts to fall off increases as the temperature is lowered, in a manner similar to PbS. The wavelengths at which sensitivity has fallen to 50% of its value on the flat portions of the curves (i.e. $1{\cdot}5\,\mu$ region) are: 90° K., $2{\cdot}54\,\mu$; 195° K., $2{\cdot}3\,\mu$. The value of the coefficient of linear expansion has been measured and found to be $\beta = 17 \times 10^{-6}$ per °C.

Hence $(dE/dT)E^{-\frac{1}{2}}\beta^{-1} = 36$, in good agreement with the values for PbS and PbTe shown in Table 2.

Capacitance Measurements on Selenium Rectifiers: Evidence of Anomalous Dispersion

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MS. received 22nd July 1949

ABSTRACT. The paper presents evidence showing that, contrary to the generally accepted view, the capacity of a selenium rectifier at audio frequencies may vary with the frequency of measurement. The magnitude of the variation depends on the metal used as counter-electrode. Thus in the frequency range 300–2,000 c/s. little variation occurs with antimony or bismuth, but with cadmium there is a considerable decrease in capacitance. The effect is considered due to polarization arising from the relative motion in the selenium lattice of the negatively charged impurity centres and positive ions which diffuse into the selenium from the counter-electrode.

IT has previously been established (Schottky 1942) that a selenium rectifier may be represented by the circuit illustrated by Figure 1. In this circuit C represents the equivalent capacitance of the barrier layer, R its differential resistance and r the resistance of the selenium layer between the two electrodes. The method generally used to determine the components of this circuit is to find the effective series resistance and reactance of the rectifier at various frequencies, the measurements being made with a small alternating voltage (less than 20 mv.) superimposed on a constant D.C. bias voltage. When the series reactance is plotted against the series resistance, a semicircular impedance locus diagram is obtained with its centre on the resistance axis. The diameter of the semicircle is equal to the barrier resistance R, and its smallest intercept with the resistance axis yields the selenium layer resistance r. The barrier capacitance C at any frequency f is given by

$$C=\frac{B}{A-r}\frac{1}{R\omega},$$

where B is the rectifier's equivalent series reactance, A its equivalent series resistance and ω the angular frequency ($\omega=2\pi f$). Both R and C depend on the D.C. bias voltage applied to the rectifier.

It follows from the semicircular locus diagram that R and r must be independent of frequency at least within limits of experimental error. It is generally supposed that C is also independent of frequency, but this does not follow directly from the existence of a semicircular locus diagram: variation of C with frequency will not cause deviation of points from the semicircle but only their shift along its circumference. The circle diameter depends only on the barrier resistance R.

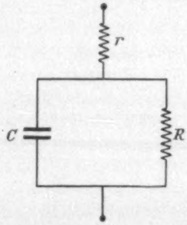

Figure 1. Equivalent circuit of selenium rectifier.

At a particular frequency the value of C determines the angle θ in Figure 3 ($\tan\theta=B/A$) and hence the point where the tip of the impedance vector Z touches the circumference of the semicircle.

Experiments made in this Laboratory have shown the circuit of Figure 1 to represent the behaviour of selenium rectifiers with counter-electrodes of bismuth and antimony. In both cases, analysis of the measurements in the frequency range 300–2,000 c/s. shows the barrier capacitance C to be sensibly independent of frequency. This is not the case, however, with rectifiers possessing cadmium counter-electrodes. The impedance locus is generally not a semicircle with its centre on the resistance axis, and thus the circuit of Figure 1 cannot be applied. However, if the D.C. bias voltage is adjusted to cause the D.C. resistance R of the barrier to decrease, the usual form of rectifier semicircular locus diagram is eventually realized. This occurs when the barrier resistance is less than about 2,000 ohms. Analysis of such a semicircular locus diagram indicates the barrier capacitance C to be a function of frequency.

Figure 2 illustrates the variation with frequency of the capacitance of a rectifier possessing a cadmium counter-electrode (area 1·3 cm²). The three curves correspond to

(*a*) the rectifier at 50° c. with +0·1 v. d.c. bias.
(*b*) the same rectifier at 20° c. with +0·1 v. d.c. bias.
(*c*) the rectifier at 50° c. with +0·04 v. d.c. bias.
(*d*) the rectifier at 20° c. with +0·04 v. d.c. bias

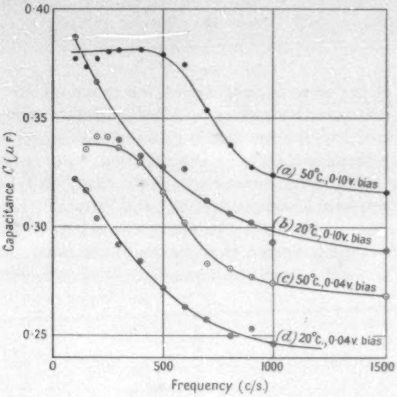

Figure 2. Variation of capacity with frequency for a selenium rectifier with a cadmium counter-electrode.

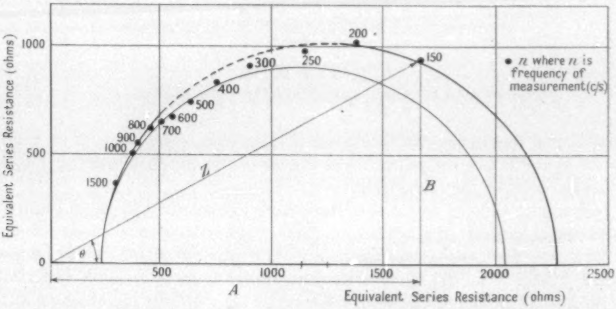

Figure 3. Impedance locus diagram. Bias volts = +0·04 volt, temperature = 50° c.

Figure 3 illustrates the locus diagram corresponding to (*c*). The impedance points in the range 250–700 c/s. do not lie precisely on the same circle as those at frequencies up to 250 c/s. and above 800 c/s. There appears to be a decrease in the value of R in the region 300–700 c/s. since the corresponding points lie on a circle (or circles) of smaller diameter. This can be accounted for by assuming the existence, in parallel with R, of a resistance R_f which is a function of frequency.

The value of R_f is comparable with R in the frequency range 250–700 c/s. but at other frequencies it is appreciably greater than R. Reference to Figure 2 shows that the above frequency range is the one in which the rectifier capacitance rapidly decreases. Therefore in order to make the circuit of Figure 1 correctly to represent the rectifier, a second resistance R_f must be added in parallel with R and C. The behaviour of C and R_f with respect to increase of frequency will be recognized as characteristic of a dielectric exhibiting anomalous dispersion, and consistent with this is the effect, exhibited in Figure 2, of temperature increase on the frequency band in which the change of capacitance occurs.

Anomalous dispersion in a dielectric is usually described by the decrease of capacitance or dielectric constant of the condenser with increasing frequency, and the accompanying changes in the tangent of the loss angle δ. For a lossy dielectric represented by a capacity C in parallel with a resistance R_f, $\tan\delta = 1/R_fC\omega$. The information contained in Figures 2 and 3 enables an estimate to be made of the maximum loss angle of the rectifier due to anomalous dispersion. The measurements made do not exactly indicate the frequency corresponding to the maximum loss angle, but in the case of the rectifier at 50° c. with 0·04 volt D.C. bias, the circle diagram of Figure 3 indicates 600 c/s. to be a reasonable value. At this frequency the capacitance was 0·3 μF. The corresponding value of R_f can be estimated from the difference in diameter of the two semicircles shown in Figure 3 and was approximately $2{\cdot}0 \times 10^4$ ohms. These figures yield a value of 0·044 for $\tan\delta_{\max}$ at 600 c/s.

At present the mechanism of the dispersion process is not fully understood but the fact that it occurred in the frequency range 200–2,000 c/s. with cadmium, but not with antimony or bismuth, shows that it is not a property of the spectroscopically pure selenium used in the preparation of the rectifiers. Recent work by Breckenridge (1948), who has observed anomalous dispersion at audio frequencies in alkali halide crystals, suggests a possible mechanism. This is that polarization results from relative motion in the selenium lattice of the negatively charged impurity centres (responsible for the defect electron conduction in selenium) and the positively charged metal ions which diffuse into the selenium from the counter-electrode.

Following Breckenridge, and applying the calculation given by Debye for anomalous dispersion and absorption in a solid, a second estimate of the maximum loss angle $\delta_{\max}$ can be made. Debye (1945) showed that

$$\tan\delta_{\max} = (\epsilon_1 - \epsilon_0)/2\sqrt{(\epsilon_1\epsilon_0)},$$

where ϵ_1 is the static or low-frequency dielectric constant, and ϵ_0 is the dielectric constant at frequencies very much higher than those at which anomalous dispersion occurs. Using values from Figure 2 curve (*c*), the above equation yields 0·115 for $\tan\delta_{\max}$. This is in reasonable agreement with the value of 0·044 previously estimated.

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On Dissociation Processes in Certain Gases of High Dielectric Strength

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MS. received 31*st August* 1949

ABSTRACT. The dissociation processes, due to electron collisions, in certain polyatomic gases such as CCl_4, CCl_2F_2 are discussed with reference to the unusually high dielectric strength of certain of these gases. Possible explanations of the latter are then suggested in terms of these dissociation processes.

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§ 1. INTRODUCTION

The high dielectric strength of certain gases, such as CCl_4, CCl_2F_2, SF_6, relative to that of, say, nitrogen, was first noticed in 1889 by Natterer (see Charlton and Cooper 1937), and has been a subject of considerable interest for some years (Joliot, Feldenkrais and Lazard 1936, Rodine and Herb 1937, Charlton and Cooper 1937, Pollock and Cooper 1939, Hochberg and Sandberg 1942). It is also a matter of some technical importance. As an example, it was found (Hochberg and Sandberg 1942) that the dielectric strength of CCl_4 vapour in certain circumstances was about 6·4 times that for air. Some relevant data are collected in the following Table.

Relative Dielectric Strengths of certain Molecular Gases

Gas	(1)	(2)	(3)
CCl_4	—	6·36	6·3
CCl_3F	3·0 (725 mm. Hg)	4·47	3–4·4
CCl_2F_2	2·4	2·56	2·4–2·5
CF_4	—	—	1·1
Cl_2	1·55	—	—
SF_6	—	2·49	2·3–2·5

(1) Dielectric strength relative to $N_2 \equiv 1$; uniform field gap, 1 atm. (Charlton and Cooper 1937).
(2) Dielectric strength relative to air $\equiv 1$; uniform field gap by extrapolation, using Paschen's law, to 1 atm. (Hochberg and Sandberg 1942).
(3) Dielectric strength relative to $N_2 \equiv 1$; as (2) (Hochberg and Sandberg 1946).

Various authors (Charlton and Cooper 1937) have endeavoured to connect the dielectric strength of such gases, as exemplified by the breakdown voltage of standard spark gaps, with various physical parameters such as molecular weight, but with little success, and no satisfactory explanation of the behaviour of the above mentioned and other similar polyatomic molecular gases has as yet been given. It has been widely known for some years that the presence of halogen atoms in the molecules of a gas is connected with unusually high dielectric strengths, as shown, for example, in the tables of data compiled by Charlton and Cooper (1937) and Hochberg and Sandberg (1942). Typical experimental work on electrical breakdown (corona or sparks) in such gases has been carried out by Charlton and Cooper (1937) and workers there cited, Pollock and Cooper (1939) (CCl_2F_2, SF_6), Hochberg and Sandberg (1942, 1946) (many gases), Craggs and Meek (1948) (CCl_2F_2), and Weissler and Mohr (1947) (CCl_2F_2/air), but possible reasons for the interesting behaviour of these gases are usually only vaguely given. Some authors (Weissler and Mohr 1947, Mohr and Weissler 1947) suggest that the free halogens (F and Cl in the case of CCl_2F_2) which are undoubtedly produced by dissociation in electrical discharges are important in that the high electron affinity of these elements (Massey 1938) will lead to the formation of stable negative ions and a resulting decrease in the free electron population in the discharge.

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It is believed that these suggestions can be supplemented or perhaps replaced after a consideration of other measurements on the halogen-containing molecular gases, but it is first necessary to discuss briefly two other general lines of investigation of their behaviour.

§2. PREVIOUS WORK ON GASES OF HIGH DIELECTRIC STRENGTH

Firstly, Hochberg and Sandberg (1942, 1946) combined measurements of sparking voltages in SF_6 with measurements of Townsend's α coefficient. This is the principal controlling factor in the breakdown voltage (Loeb and Meek 1940), especially for breakdown in the streamer régime, i.e. for $pd>200$ say, where p is the pressure in mm. Hg and d the discharge gap length in air. Thus, Meek's equation giving the breakdown field X_s in a spark gap for conditions in which the streamer mechanism applies is

$$X_s(d/p)^{\frac{1}{2}} = K\alpha e^{\alpha d}$$

for a uniform field gap. Hochberg and Sandberg show that the value of α in SF_6 is very low compared with that in air (at X/p 115–122, $\alpha(SF_6) \simeq 1/30\ \alpha(\text{air})$) and proceed to suggest that the low value of α agrees reasonably with the high breakdown voltage in SF_6 (2·5 times that of air, in the conditions cited (Hochberg and Sandberg 1942)) on the basis of Meek's equation (Loeb and Meek 1940, Meek 1940). Hochberg and Sandberg (1946) later extended the measurements of α to include C_2H_5Cl, C_2H_5Br, C_5H_{12}, SF_6 (as a check on the earlier results), $CHCl_3$ and CCl_4. The highest values of X/p for a given α/p occur for $CHCl_3$ and CCl_4, and it is shown how high values of breakdown voltage are related to low values of α/p for all the gases studied. It is suggested that these low values of α are due to higher electron energy losses in inelastic non-ionizing collisions which should be more frequent with complex polyatomic molecules, but it then seems difficult to understand why relatively complex molecular gases, e.g. C_5H_{12}, should not have lower values of α than is the case.

Secondly, studies of dissociation processes due to electron collisions in several gases such as SF_6 (Dibeler and Mohler 1948), $SiCl_4$ (Vought 1947), SiF_4 (Dibeler and Mohler 1948), CCl_4 (Baker and Tate 1938, Warren and Craggs 1949), CF_4 (Dibeler and Mohler 1948, Warren and Craggs 1949), $CClF_3$ and $CFCl_3$ (Warren and Craggs 1949) have given results of considerable interest and complexity which have not previously been invoked in suggested explanations of the low value of the Townsend α in certain of these gases. Vought's study of the dissociation products of $SiCl_4$ appears to be the most complete analysis of its kind; he found the following reactions, amongst others, which may be of importance in the present connection, and which are given here as examples of certain general types of collision processes (Massey 1938).

$$\left.\begin{array}{ll}(1a) & \mathrm{SiCl_4+e\rightarrow SiCl_3+Cl^-} \\ & \mathrm{SiCl_4+e\rightarrow SiCl_2+Cl+Cl} \\ & \mathrm{SiCl_4+e\rightarrow SiCl+Cl_2+Cl^-} \\ & \mathrm{SiCl_4+e\rightarrow SiCl+2Cl+Cl^-} \\ (1b) & \mathrm{SiCl_4+e\rightarrow Cl_2+SiCl_2^-} \\ & \mathrm{SiCl_4+e\rightarrow 2Cl+SiCl_2^-} \end{array}\right\}\text{Electron capture, followed by dissociation.}$$

$$\left.\begin{array}{ll}(2a) & \mathrm{SiCl_4+e\rightarrow SiCl_4^{+}+e+e} \\ (2b) & \mathrm{SiCl_4+e\rightarrow SiCl_3^{+}+Cl+e+e} \end{array}\right\}\text{Ionization, with production of free electrons.}$$

$$\begin{array}{ll}(3) & \mathrm{SiCl_4+e\rightarrow SiCl_3^{+}+Cl^-+e} \end{array}\left\{\text{Dissociation into negative ion and positive ion.}\right.$$

All these processes, especially (2*a*), have long been known and studied, and Massey has given a particularly clear discussion of (1) and (3) with special reference to the case of oxygen. (1*a*) can occur at very low energies (~1 ev.), particularly if the electron affinity of the atom forming the negative ion is high and if the energy required to dissociate the molecules is low. The process (3) usually requires an electron energy close to that for (2*a*). There are, of course, other dissociation products formed at higher energies. It has been found that for all the gases listed in the last paragraph, except $SiCl_4$, the reaction (3) is very much more probable than (2). Thus, for example, Dibeler and Mohler (1948) estimated that if I is the current, $I(SF_5^+)/I\,(SF_6^+)$ at 50–100 ev. was 5,000 : 1 and that $I(SiF_3^+)/I(SiF_4^+)$ was about 50 : 1 at 50–100 ev. Warren (Warren and Craggs 1950) was unable to detect $I(CCl_4^+)$ in a case where $I(CCl_3^+)$ was easily measurable. Baker and Tate (1938) quote similar data for CCl_4 and CCl_2F_2. For the exceptional case of $SiCl_4$ (Vought 1947), $I(SiCl_3^+)/I(SiCl_4^+)$ was 100 : 56 at 75 ev. It has not been found possible to calculate the relative probabilities for reactions (2) and (3) in the present cases of polyatomic molecules.

§ 3. ELECTRICAL CHARACTERISTICS OF FLUOR- AND CHLOR-CARBONS

The low values of Townsend's α for SF_6, CCl_4 etc. may be due partly to the molecular complexity and, therefore, to the greater possibility of inelastic non-ionizing collisions, although this cannot be the sole explanation since other complex gases give larger values of α. Free halogens are produced by dissociation (see reaction type (1)), and thus attachment can result with a resulting loss of free electrons, but this should also occur in Cl_2 and O_2 which show a 'normal' value of dielectric strength (Charlton and Cooper 1937, Stephenson 1933). Negative molecular ions can, of course, also occur in these simple gases. It would appear also that process (1), which occurs in O_2 (Massey 1938), is not primarily responsible for low values of α, although it must be made clear that the probability of electron capture (process (1)) might be unexpectedly great for the complex molecules. However, the relative scarcity of the primary ion (process (2*a*)) with respect to the yield of higher products of ionization (process (3)), which has been observed for SF_6, CCl_4, etc., is a characteristic of this type of molecule (see, however, the work of Stevenson and Hipple 1942). It is to be expected that this might in turn lead to low values of α since, unless the electric field in the discharge is high enough to cause electron detachment by collision (Massey 1938), no contribution to a

Townsend avalanche can be made by a reaction of type (3). Thus the inefficient production of fresh electrons by process (2 *a*) should lead to the observed low values of α, which in turn (Hochberg and Sandberg 1946) lead to high dielectric strengths. In the case of chlorine and fluorine negative ions the fields necessary to cause detachment would presumably need to be much greater than that corresponding to $X/p = 90$ v/cm/mm. Hg (Massey 1938), since this appears to be the necessary value in molecular oxygen which has an electron affinity probably about 0·2 ev. and therefore appreciably less than that of chlorine or fluorine.

It will be noticed that there are large variations of dielectric strength and therefore of Townsend's α even amongst gases which are alike in that they show little tendency to form the primary ion; thus CF_4 (Hochberg 1947) has a dielectric strength close to that of N_2, although (Dibeler and Mohler 1948) CF_4^+ is hardly detectable compared with CF_3^+ in the products of dissociation due to electron bombardment. Further, CCl_2F_2 and CCl_4 (Charlton and Cooper 1937, Weber 1942) have respectively about 2·5 and 6 times the dielectric strength of air or N_2 (for the particular conditions of the experiments cited), and both (Baker and Tate 1938) show very little tendency to form the primary ion (i.e. $CCl_2F_2^+$ or CCl_4^+). It is suggested that these variations may be due to the relative probabilities of reactions of types (2 *b*) and (3), and that for the gases with the highest dielectric strength (CCl_4) reaction (2 *b*), which would of course contribute to a Townsend α, is relatively improbable. Evidence is provided in support of this by the work of Baker and Tate (1938), whose results show that, if we make the apparently reasonable assumption (Massey 1938) that resonance capture of electrons, leading to reactions (1 *a*) and (1 *b*), is relatively negligible, the probabilities of the occurrence of reaction (3) compared with that of reaction (2 *b*) in CCl_4 and CCl_2F_2 respectively are (at 75 ev. electron energy) about 100 : 1 and 100 : 16. It seems possible, therefore, that reaction (2 *b*) would still be more probable in CF_4.

The reaction (2 *b*) should be produced at a higher appearance potential than reaction (3), as Vought (1947) pointed out, by an amount, 3·8 ev, equal to the electron affinity of, in this case, chlorine. Its onset was not noticed by Vought or mentioned by Baker and Tate, but this may be due to the large positive ion current found at about 3·8 ev. above the appearance potential for (3). It is clear that measurements of negative and positive ion currents at energies just above the critical values are needed, and we propose to undertake this work.

The well-known fact (Charlton and Cooper 1937) that addition of CCl_4 or CCl_2F_2 (Weber 1942) to, say, N_2 gives an appreciably increased dielectric strength, is presumably due to the above mechanisms, since the critical potentials for these processes in CCl_4 or CCl_2F_2 are lower than the ionization potential for N_2, and thus the electron temperature in any discharge in, say, N_2/CCl_4 is lowered compared with that in N_2. It would thus appear possible that additions of SF_6 to N_2, or of CCl_4 to Xe might not give rise to appreciably increased dielectric strength, and these experiments will shortly be carried out in these laboratories.

In conclusion, it may be stated that whilst the suggested mechanisms seem to explain qualitatively the known experimental data, it is essential to check the existing scanty information, particularly on negative ion yields at various bombarding electron energies, especially for reaction (3) as compared with reaction (2 *b*), and to extend it. This work will be carried out in these laboratories and preliminary experiments on the appearance potentials for various reactions (Warren and Craggs 1949) have now been in progress since October 1948 in our mass spectrometer laboratory. Further experiments on the dielectric strength of certain mixtures, on measurements of Townsend's α and on the investigation of dissociation products formed in electrical discharges are in hand in the Electrical Engineering Laboratories.

§4. SUMMARY

It is suggested that the dielectric strengths of the well-known chlor- and fluor-carbons, and of certain related compounds, such as SF_6 can be explained in terms of certain general dissociation reactions:

$XY_n + e \rightarrow XY_n{}^+ + e + e$ ......(A) referred to as (2*a*) in text

$XY_n + e \rightarrow XY^+_{n-1} + Y^- + e$ ......(B) referred to as (3) in text

$XY_n + e \rightarrow XY^+_{n-1} + Y + e + e$ ......(C) referred to as (2*b*) in text

where X is usually an atom of carbon or sulphur and Y is a halogen atom, usually in the most useful gases, of chlorine or fluorine or combinations thereof. Examples of the latter are $CClF_3$, CCl_2F_2 and CCl_3F, which we have studied, and in which the most important of reactions (B) and (C) are those in which the escaping Y atom is chlorine. It is known that the values of Townsend's α coefficient, which, in given geometrical conditions and particularly at high pressures, largely determines the dielectric strength of a discharge gap (Hochberg and Sandberg 1946), are very low for CCl_4, CCl_2F_2, SF_6 etc., and also that in such gases the reaction (B) is much more probable than reaction (A). It is suggested here that since reaction (B) does not provide new electrons, as would reactions (A) or (C), the resulting value of Townsend's α would necessarily be much lower than in simple gases such as H_2 or Ne.

It is also known that the dielectric strength of the halogen derivatives of methane show progressively falling dielectric strengths as the Cl atoms in CCl_4 are successively replaced by F atoms, and indeed that CF_4 has a dielectric strength relatively little different from that of air. It is suggested that this is due to the increasing importance of reaction (C) compared with reaction (B) as the dielectric strength decreases. The available data (Baker and Tate 1938, Vought 1947) support the above suggestions but, clearly, much more experimental work is required to check the proposals. Various aspects of this work are now being studied in these laboratories.

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The Static Coefficient of Friction and the Area of Contact

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ABSTRACT. An apparatus for measuring the static coefficient of friction has been designed in which the forces tending to disturb the contact area are minimized and which further enables the contact area to be viewed throughout the experiment. Application of a tangential load, less than that required to give limiting friction, has been shown to give rise to a growth of both the real and apparent contact areas and to produce a relative displacement of the surfaces to an extent governed by the tangential load. An examination of the surface topography, by means of an electron microscope, has shown that the earlier type of slip ceases because surface scratches extend the boundaries of real contact. Both the force of adhesion and the tangential force vary linearly with the real and apparent areas of contact. These results are in accord with a cohesive theory of friction, and offer no support for the theory on which friction is attributed to the formation of welded junctions.

§1. INTRODUCTION

When attributing the force of sliding friction between solid bodies to the raising of one member over the surface irregularities, or asperities, on the other, Coulomb (1785) discounts the explanation of cohesive force on the grounds that it was not in accordance with his experimental observations that friction is independent of the area of contact. The existence of strong cohesive forces was nevertheless later postulated by Hardy (1936) in his work on static friction, and he found evidence for it in such effects as the doubly refracting nature of pieces torn from a glass slider.

There has been a reluctance to accept a purely cohesive theory of friction, since our knowledge of elastic deformation has been insufficient to explain the observed proportionality between the normal load and the real area of contact. This difficulty remained until Bowden and Tabor (1939) claimed to have shown that the surface irregularities deformed plastically in such a way that the real area of contact was proportional to the normal load. Although Bowden and co-workers recognized that bulk properties of the bodies and their surface dimensions

(Bowden and Hughes 1939) played an important rôle in friction, they nevertheless believed that the major contribution arose from welding of the surfaces at their points of contact (see Bowden and Tabor 1945). An objection has, however, been lodged by Bickerman and Rideal (1939), who showed that it was not, in general, possible to reduce the normal load between two bodies without also decreasing the real area of contact, and, therefore, the force of friction. This, they claimed, was contrary to the conception of plastic flow and cohesion. In reply, Bowden and Leben (1940) pointed out that beyond the boundary of plastic flow there exists an elastic strain which, when released by a reduction in the normal load, would sever many of the points of contact. They also suggested that, as the strain produced by the tangential pull could not be equally shared by all the points of contact, the friction must be determined by the load actually applied during the measurement. Nevertheless, failing further evidence on the relation between force of friction and the real area of contact, Bickerman (1948) and Gemant (1943) still adhere to Coulomb's asperity theory of friction.

In view of the rival claims of the asperity and cohesion theory, it was felt that more experimental evidence was needed to dispel, once and for all, the belief that the asperity theory constituted in itself an adequate explanation for all friction phenomena. The work described in this paper purports to do this, and at the same time provides new information on the dependence of the tangential force of friction on the real area of contact.

For an investigation of this kind elastic materials are unsuitable, since the real area of contact is determined only by the normal load and so does not enable the effects of these two quantities on friction to be separated. There are, fortunately, materials for which change in area of contact may be brought about without change of normal load. For instance, the area of contact between hemispheres made from material of low yield point, such as lead or indium, is a function of the arithmetic sum of the magnitudes of the curvatures of the two surfaces. The area of contact of materials such as lead may also be varied, independent of normal load, by a hysteresis effect which is exhibited on increasing and decreasing the normal load. Preliminary experiments, using the latter phenomenon, showed that the coefficient of friction as normally defined can be increased by 100 per cent, and although these results were only qualitative, they were regarded as sufficiently encouraging to warrant the construction of apparatus for quantitative work.

§ 2. APPARATUS

The design of the apparatus presented the problem of sliding one surface over another without the introduction of any force which might tend to disturb the area of contact. It was also considered desirable to incorporate means for viewing the area of contact throughout the experiment. These requirements demand parallel motion of the sliding surfaces, an arrangement to prevent tilting of the fixed surface, and the use of a transparent material for at least one friction member.

The essential features of the apparatus designed to meet these conditions are shown diagrammatically in Figure 1. Parallel motion of the sliding surfaces is achieved by the use of two glass optical flats, A and B, separated by a thin film of oleic acid. The upper flat, A, was rigidly mounted on an aluminium plate 6 mm. thick, and the lower flat, B, which serves as one friction member, was kept in equilibrium by the second friction member, C, which was thrust upwards by the normal friction force. For the quantitative work described in the first part of this paper the normal load was maintained sufficient to support the weight of the lower optical flat (40 gm.) and to maintain the thickness of the oleic acid film constant for the duration of the experiment. For the latter work, carried out with an electron microscope, the normal load was increased up to 240 gm. The normal load was applied by means of a string in tension that pulled up a triangular frame, D, whose apex supported the second friction member C (mounted in wax), while to the base of the frame was fitted a rod which rolled in Vee blocks spaced 20 cm. apart. By these means tilting of the friction members was reduced to a minimum. The movement of flat B was effected by light cords attached to the framework E, which was built around the flat in such a manner that the plane of pull was near to the plane of sliding. The cords passed over three pulleys as shown, and were kept in tension by equal weights attached to the free vertical lengths. It was found convenient to apply the frictional forces by means of suspended beakers into which was poured water, accurately measured on completion of the experiment. In some of the experiments it was required to restrict the slip to a pre-selected value, and this was done by limiting the movement of the framework by means of the anvil of a bench micrometer capable of detecting displacements of 0·5 micron. Contact between the framework and the anvil was indicated electrically.

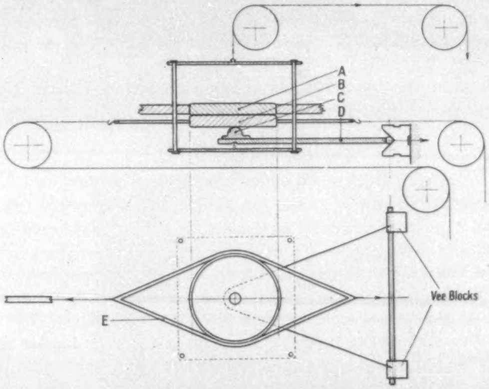

Figure 1. Diagram of apparatus.

With the above arrangement the area of contact was viewed through a microscope fitted with a $1\frac{1}{2}$ in. objective, and an eyepiece that was fitted with a measuring micrometer calibrated to 2·5 microns. Vertical illumination was used.

To prescribe the area in which contact occurred the friction member, C, was made in the form of a hemisphere. Experiments were carried out with lead and indium of Analar purity. The specimens were made by pouring molten metal from a crucible into hemispherical impressions, which had been formed by pressing ball bearings into a polished $\frac{1}{4}$ in. thick copper plate. The metal poured cleanly, and on solidification its surface was characterized by a regular system of fine cooling ripples (see Graf 1942) similar in appearance to the undulations left on sand by a receding tide. Their distance of separation was approximately 3 microns.

§ 3. EXPERIMENTAL TECHNIQUE

The flat B was first removed, and its lower surface polished with a piece of mutton cloth that had been degreased by extraction with trichlorethylene in a Soxhlet apparatus. The polishing was continued until the contaminating films were sufficiently thin and homogeneous. The latter condition was judged by breathing upon the surface and noting the appearance on the resulting grey film. At this stage a drop of oleic acid was placed on the reverse side and the flat remounted in position. The drop was then spread into a film by rotating and pressing the lower flat upwards, after which it was centralized with respect to the upper flat. Measurements throughout the course of this work showed that the force required to move the flat never exceeded 3 gm. The lead hemispherical member was finally fixed in position, and then slowly moved into contact with the glass.

Initial experiments showed that the apparatus was extremely sensitive to vibration, and vertical oscillations that were transmitted to the friction member gave contact areas far in excess of those required to support the normal load. Indeed, despite the fact that the friction surfaces must have collected a considerable amount of contamination from the atmosphere, values of μ could not be obtained less than unity. The effect of vibration was, however, progressively reduced by partially insulating the apparatus on rubber pads and replacing the light cords by elastic strings. Figure 2* shows a general view of the apparatus.

§ 4. EXPERIMENTAL

(i) *Friction Force and the Area of Contact*

Examination of the contact area, formed by placing the $\frac{3}{8}$ in. diameter hemisphere of lead in position against the glass flat, showed that the resultant distortion did not materially alter the appearance of the cooling ripples or crystal boundaries. In fact these features were still preserved when the hemisphere was distorted to a disc of thickness approximately one-quarter of the original diameter. The preservation of the surface flaws has been attributed by Moore (1948) to the tips of the asperities undergoing work-hardening and so being harder than the bulk material. This explanation, however, does not seem applicable to this work, since systems of slip bands were observed to traverse the real area of contact and neighbouring valleys without any perceptible change in direction or spacing. The bands merely appeared to be flattened by contact with the glass. Although it was not found possible to obtain a clear photograph of this behaviour, the form of slip bands is illustrated in Figures 3 and 4 (Plate). Figure 3 shows a general view of the contact area, and the slip bands are to be seen as criss-cross lines at the bottom left-hand corner. Other slip bands can be seen at the top right-hand corner. Figure 4 shows an enlargement of slip bands that lie in a valley within the apparent area of contact. In the top left-hand corner all surface features are obliterated by slip, but in the top right-hand corner slip bands can be seen to cross, undeviated, a small plateau. Notwithstanding this preservation of surface identity, the boundary of contact was clearly defined, and was taken as that located by the inner ring of a system of fine interference fringes. On applying a tangential load two unexpected features were observed. The apparent area of contact increased with the tangential load, and this was accompanied by a gradual obliteration in the surface features (see Figure 3). These changes continued until the tangential load was sufficient to cause slip. The term is here used to denote

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* For Figures 2–4, 7 and 8 and 11–16, see Plates.

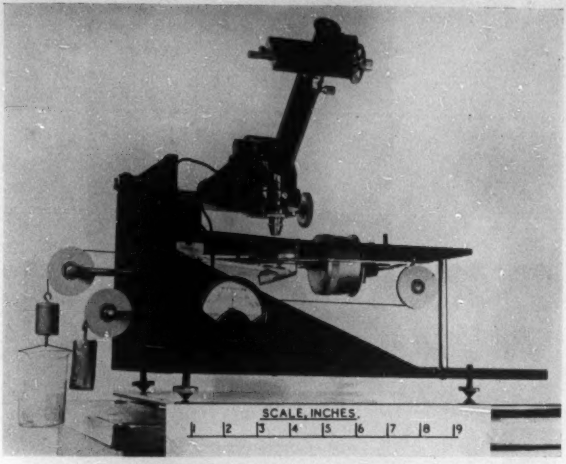
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Figure 2. General view of apparatus.

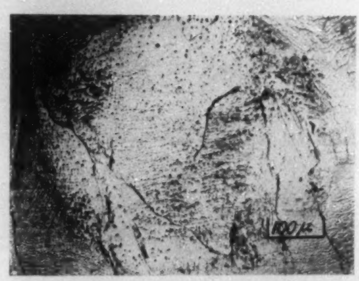
100 µ
Direction of motion

Figure 3. Apparent area of contact between $\frac{3}{8}$ in. diameter lead and glass flat after an interfacial movement of 25·4 microns. Vertical illuminations.

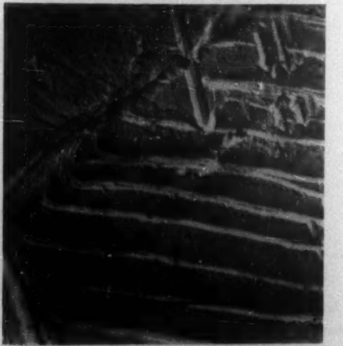
Direction of motion

Figure 4. Slip bands at higher magnification.

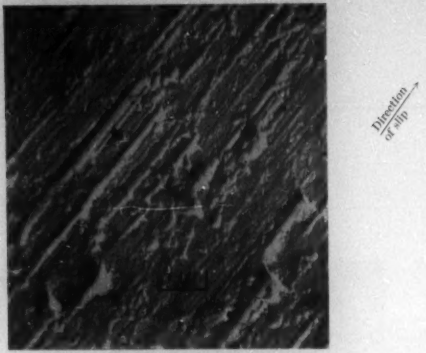
Direction of slip

Figure 14. Contact area covered with scratches.

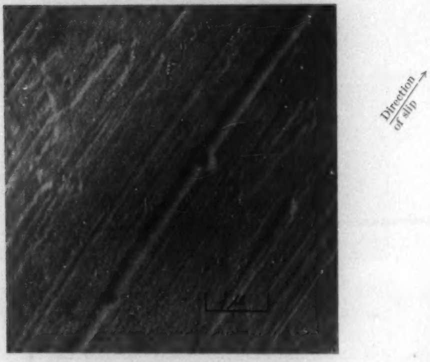
1 μ
Direction of slip

Figure 15. View showing nature of scratches.

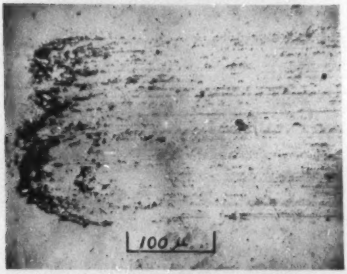

Figure 16. Deposit of lead on glass flat after sliding $\frac{1}{8}$ in. diameter lead hemisphere at a normal load of 40 gm.

the point at which the tangential force is sufficient to cause continuous sliding, and in what follows will be referred to as macroslip.

A few measurements of the tangential frictional force for the ⅜ in. diameter lead specimen showed considerable scatter, and an attempt was therefore made to see whether cleaner conditions might lead to greater experimental consistency. The apparatus was obviously unsuitable for use with physically clean surfaces, since the film of oleic acid was too near the friction surface and could not be easily isolated. Strong (1938), however, has described a method whereby chemical cleaning can be obtained by the use of a blowpipe flame or an electric spark. Accordingly the discharge from an 'Edwards' vacuum leak detector was played over the friction surface for a few minutes at atmospheric pressure, and this produced a surface associated with a very high friction that was sufficiently persistent to withstand exposure to the atmosphere for some hours. The high friction of this cleaned surface was also accompanied by a corresponding increase in the area of contact that took place during the increase in the tangential load, and its nature was such that if the experiment was held up at any point prior to slip, the ratio of the area to the applied tangential load was constant.

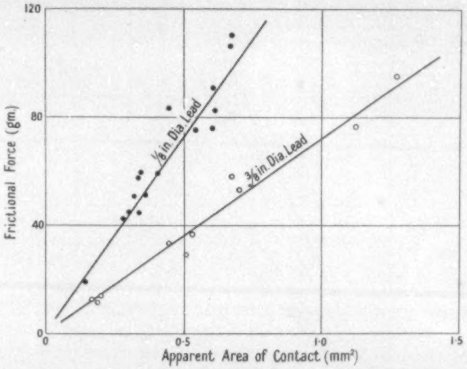

Figure 5.

A variation in the apparent area of contact for the normal load of 40 gm. was obtained by removing the vibration insulation in the apparatus and replacing it in gradual stages. By this means an eightfold increase in area was obtained. A series of measurements was then made of the tangential friction force for the range of contact areas, and the results are shown in Figure 5. It will be seen that there is a linear relationship betweeen tangential force and the apparent area of contact. Results for the ⅛ in. hemisphere show the most scatter, but even here a correlation coefficient of 0·98 for the above variables showed the relationship to be significant.

It may be recorded, as a matter of interest, that various experimental techniques were tried out in an attempt further to minimize experimental scatter, but in all cases the correlation coefficient remained approximately the same. A part of this scatter may be attributed to any remaining instability of contact, since any minute displacement of the friction surface would tend to allow the contact area to regain its value associated with the normal load of 40 gm. The variation of friction with crystal direction is also likely to contribute to the scatter, especially as the crystal size of the lead and indium was observed to be of the same order as the contact area. In this connection Gwathmey, Leidheiser and Smith (1948), working with single crystals of copper, have noted a fourfold variation in the static friction with crystal direction.

The relation shown in Figure 5, i.e. that the tangential friction force is proportional to the apparent area of contact, is contrary to Amontons' law and to general experience. If the friction force is attributable to cohesive forces, it is to be expected that the tangential friction force will be proportional to the real area of contact, and for this to be possible the ratio of the apparent to the real area of contact must have been constant. However, any assumption on the nature of friction is, at this stage, unwarranted, and further experiments were therefore made to see whether the same law held in absence of the tangential load. To this end, lead and indium hemispheres of varying radii were compressed under a range of normal loads and the apparent contact area measured. The results are shown in Figure 6, where the apparent area of contact is seen to vary linearly with normal load. This result is in accord with the assumption of a constant ratio for the apparent to the real area of contact, since it is to be expected that for these materials the real area of contact will be proportional to the normal load. For a given material at a given load, the apparent area of contact was found to be dependent on the total change in curvature of the contact faces during deformation.

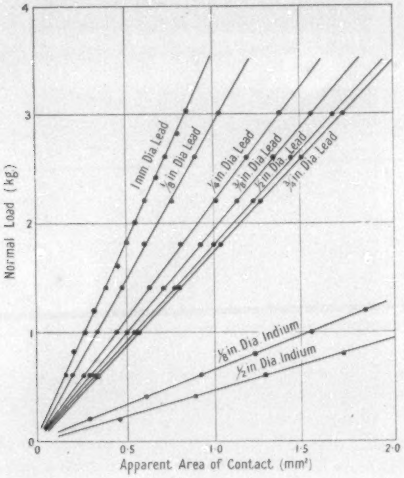

Figure 6

During the process of slip the original apparent contact area on the glass underwent a change in surface properties. This was shown by the fact that if the lead was returned over the same track immediately after macroslip, a sudden increase in the degree of scratching occurred as soon as the lead re-crossed the boundary of orginal contact area. This increase in scratching was accompanied by an increase in the friction force and the apparent area of contact. In the first traverse of the lead, contaminating films must have been wiped from the original contact area and smeared over the track. The exact nature of this phenomenon depended upon the original state of cleanliness of the glass surface.

(ii) *Adhesion*

The surfaces cleaned by the electrical discharge were characterized by measurable forces of adhesion. With lead the adhesive force was small compared with the normal load, but with indium the adhesive force was so great that sliding produced very great distortion. The indium behaved as a plastic material in that even with a small normal load the area of apparent contact could be increased indefinitely on applying a tangential load. In Figure 7 (Plate) is shown the contact area formed between a $\frac{1}{8}$ in. diameter indium hemisphere and glass for a tangential load of 2,500 gm. and a normal load of 40 gm. The position of the original area before application of the tangential load is shown outlined. One half only is shown, since the other portion became detached on removing the indium from the glass prior to taking the photograph. In Figure 8 is illustrated a section taken through AA, showing that not only is the shear strength of the material exceeded near the surface, but for some way down. These experiments were satisfactorily repeated in an atmosphere of pure hydrogen, which showed that the wetting of the glass by the indium was not due to the formation of an oxygen bond (King 1942). It may be remarked that previously recorded cases of high adhesion have required either high temperatures (Schnurmann 1941) or outgassing at high temperatures under vacuum (Bowden and Hughes 1939).

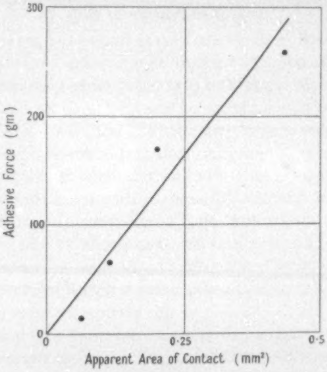

Figure 9.

The adhesion values of a $\frac{1}{8}$ in. diameter hemisphere of indium were measured against glass, and the results given in Figure 9 show the adhesion force to be linear with the apparent area of contact. In this experiment the glass was not electrically cleaned, and the area of contact was produced by applying a tangential force with a 40 gm. normal load. Since it is reasonable to expect that adhesion will be proportional to the real area of contact, this relation again confirms the consistency of the ratio of the real to the apparent area of contact.

When Hardy postulated his cohesive mechanisms of friction he pointed out that resistance to displacement of the surfaces along the tangent, but not along the normal, could be expected, since separation along the normal involved the progressive peeling away of the surface. In the case of the compressed hemisphere, any tendency towards recovery is concentrated at the edge of the contact disc over an annulus of a thickness that depends upon the effective range of the surface forces. Although for indium this force of adhesion may be of the same order as the normal load, it does not materially influence the area of contact owing to the short-range nature of these forces. That this is so is demonstrated by the fact that the linear relation shown in Figure 5 is not disturbed by the fact that only certain of the observations were associated with high adhesion values.

(iii) *The Nature of Slip*

To study the growth in the contact areas due to the application of a tangential load it was decided to conduct friction experiments on lead with the tangential load restricted to a small fraction of that required to give macroslip, and to study the appearance of the contact areas on the lead with an electron microscope.

The electron microscopy was carried out with a Metropolitan-Vickers 50 kv. EM.2 tube used in conjunction with a replica technique and gold shadowing. The choice of replica technique was limited owing to the low melting point and softness of the lead, and by the difficulty of dissolving the metal away from such materials as silica. Difficulties also arose from the curvature of the metal surrounding the contact area and the magnitude of the surface irregularities. The former tended to cause bad wrinkles in the film. The technique adopted was to use simple negative replicas formed from a dilute solution of polyvinyl formal and ethylene dichloride. The size of the surface features and the curvature of the hemispheres demanded a half per cent solution which corresponds to a film thickness in the range of 1000 to 2000 A. The replicas were formed by immersing the hemispheres in the formal solution, after which they were shaken to remove surplus solution and allowed to dry for about five minutes. Two lines were then cut by means of a razor through the replica into the lead in the direction of strain. The replica was removed from the lead under distilled water by folding the film back on itself with the aid of a pair of fine forceps. The surface replicas were then floated, impression side upwards, and set in position on a sample grid. After drying for several hours in a desiccator, the replica was shadowed, at right angles to the direction of frictional strain, with gold atoms at an angle of $\tan^{-1}\frac{1}{4}$ to a calculated depth of 90 A.

It was planned to begin by obtaining electron micrographs of the lead surface corresponding to an applied tangential load one-tenth of that required to give macroslip. In this experiment, however, it was noticed that even with this applied load some slip took place, and it was therefore decided to study its mechanism in more detail before examining the contact areas. A few subsequent experiments showed that the extent of this slip was determined by the tangential load, and that it was accompanied by a large visual change in the magnitude and distribution of the real area of contact, the nature of which must have restored equilibrium. This dependence of slip upon the tangential load suggested the feasibility of limiting the slip rather than the tangential load, and the projected experiments were modified in that the bench micrometer was used to increase the slip in steps of 6·35 microns up to a total of 63·5 microns. This latter value was in the neighbourhood of that required to give macroslip. The observed relation between the tangential load and the distance slipped is shown in Figure 10. The point of macroslip, corresponding to static friction as normally measured, is shown by the dotted line, and will be seen to have been approached slowly. This unambiguous determination of the static coefficient of friction is contrary to the view expressed by Bristow (1947).

An examination of the surface of the lead hemisphere throughout these experiments revealed changes in contact areas which, in conjunction with a cohesive theory of friction, satisfactorily accounts for the progressive nature of slip. In the absence of a tangential load the tips of the asperities supported the load elastically, and the electron microscope revealed no evidence of permanent deformation of the asperities. In fact the shape of the asperities was so well preserved that, on removing the normal load, gold shadowing failed to record any change across the contact area. When, however, a tangential load was applied equal to 10 per cent of that required to give macroslip, the asperities deformed plastically into small plateaux within the apparent contact area. Figure 11 (see Plate) shows an electron micrograph of the lead surface before being placed in contact with the glass, and Figure 12 shows the surface after a slip of 6·35 microns. The tips of the asperities were always scratched, which showed that interfacial movement has occurred, and in Figure 13, corresponding to a slip of 25·4 microns, the scratches are seen to extend up to the boundary dividing the real and apparent areas of contact. With further increase in the tangential load a proportional increase took place both in the slip and in the growth of the real area of contact, and eventually the whole of the apparent area of contact

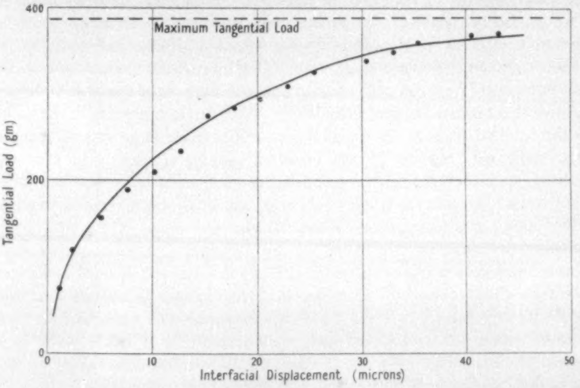

Figure 10.

had contacted the glass and had become covered with scratches (Figure 14). At this point the tangential load reached its maximum value and macroslip ensued. The nature of the scratches is shown in Figure 15 in which they are seen to consist of parallel furrows without any indication of pile-up of displaced material.

§ 5. DISCUSSION

The mechanism of slip has been revealed in greater detail than hitherto, and the sequence of the changes in contact area, and the effect of such changes on the tangential frictional force, can now readily be visualized from the moment of placing the two bodies in contact. When the lead or indium hemisphere is pressed against the flat hard surface bulk plastic deformation occurs, but the surface irregularities are preserved and the tips of the asperities undergo a deformation which is mainly elastic. The real area of contact is proportional to, and increases with, the normal load. Momentary increase of the normal load, such as occurs from vibration, can give rise to a permanent increase in the real area of contact, provided there are no extraneous disturbing forces such as would result from tilting. If to one of the two contacting surfaces a tangential pull be gradually applied, the surface will presumably undergo some elastic deformation due to conservative forces (Rankin 1926), followed by plastic deformation of asperities and an accompanying increase in the real area of contact. These latter two features will occur when the tangential force is only a small fraction of that required to give macroslip. With further increase in the tangential force the original areas at the tip of the asperities become scratched and grow in extent, while new regions of real areas of contact appear. This process of scratching, with increases in the real areas of contact, continues with increase in the tangential load until the whole of the real contact area is covered with scratches, at which point macroslip takes place. If the real areas of contact have been artificially increased by vibration, or by hysteresis occasioned by previous increasing and decreasing of the normal load, the magnitude of the changes will be correspondingly reduced. It is due to these changes in contact area that slip takes place progressively. Thus if a small tangential load less than that required to give macroslip be applied, an out-of-balance system of forces is set up which gives rise to slip. This only ceases when equilibrium is restored by an increase in the cohesive forces that are brought about by a growth in the real area of contact. It is when further growth cannot take place by reason of external geometrical features that slip becomes unlimited.

Throughout all stages up to macroslip the tangential load was found to be proportional to the apparent area of contact, and therefore also proportional to the real area of contact since the ratio of the two areas was deduced to be constant. The concept of frictional force per unit of real area of contact has previously been used by Holm (1938), who termed it the specific force of friction. This manner of expressing the results is obviously more desirable here than the use of the coefficient of friction, for the latter involves the normal load and so introduces confusion.

Observations through the light microscope showed no visible scratching before macroslip, whereas with the electron microscope scratching was apparent throughout. There is no reason to doubt that scratching commences from the moment the conservative forces are exceeded, and this being so, it is difficult to appreciate the distinction made by Schnurmann (1941) and by Bickerman (1948) between sliding with scratching and sliding without. To restrict Amontons' law, and even the term friction, as these writers suggest, to sliding that occurs without permanent deformation places an unwarranted emphasis on an arbitrary criterion as to whether or not scratching is visible to the naked eye.

An examination of the formation of scratches with the electron microscope shows a number of important features. With the smallest observed slip there were small particles of lead adhering to the glass plate. In illustration of this mechanism, Figure 16 shows lead particles adhering after a slip of 3 mm., while the shadow replica technique from the lead showed that the particles had ploughed parallel-sided furrows in it without any change in the size of the particles. These furrows, moreover, had no lead piled up at their sides, so that the displacement of lead must have occurred by means of transference through the bulk of the material. That this did in fact occur was confirmed by changes in the appearance of the contours of the isolated contact areas through scratching. On the application of a tangential load only one-tenth per cent of that required to give macroslip, areas containing scratches were changed to small plateaux standing in sharp relief to the general background. Figure 17 illustrates a cross section of the apparent contact area and indicates the manner in which the surface topography can be altered by scratching. In (*a*) the contact angle is much less than $\tan^{-1} \frac{1}{4}$, so that the shadow is indefinite. In (*b*), however, the metal displaced from A to B increases the contact angle and so gives rise to sharp relief. The growth in the real area of contact is thus seen to depend upon the depth of the scratch and the angle of contact at the boundary. The fact that scratching is associated with bulk deformation through the material renders any attempt to estimate the quantitative contribution of scratching to the force of friction very difficult. It is to be noted in passing that the ploughing term discussed by Bowden, Moore and Tabor (1943) is not apposite, since their experiments and calculations assumed incorrectly that metal is piled up at the edge of the ploughed furrow.

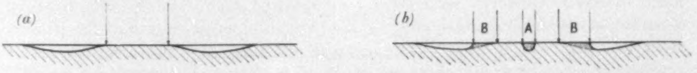

Figure 17.

(*a*) Section through contact area before application of tangential load, showing the tip of one asperity in contact with the glass.

(*b*) After the application of tangential load, showing the volume of metal displaced by scratching to form more contact area.

The preservation of asperities during deformation of relatively hard metals has been described by Moore (1948), although there has been a general belief that plastic deformation of non-conforming materials leads to a coincidence of the real and apparent contact area (see for example Blok (1940)). This belief, here demonstrated to be false, seems to have been held by Bowden and Tabor (1939) in their work on the area of contact between stationary and moving surfaces. These authors measured the area of contact between crossed cylinders by conductance methods, and by microscopic observations of the indentation left after removal of the normal load. The reason they were able to deduce correctly the ratio between the normal load and the real area of contact is shown by this work to be attributed to the constant ratio of the real and apparent area of contact. Their agreement between the electric and visual measurements is explicable in that the passage of electric currents is not necessarily limited to the restricted areas of close contact but may occur over gaps (Frenkel 1945, 1946). Confirmatory evidence that Bowden and Tabor's crossed cylinders gave rise to apparent contact areas is adduced from the fact that they found it necessary to resort to tapping in order to obtain consistent results. They attributed this effect to the crushing-out of contaminating films, whereas the true explanation would seem to be that the real areas of contact did actually increase. This explanation, moreover, agrees with their observation that reduction in the normal load gave a drop in conductance. Bowden and Leben put forward a tentative theory involving the growth of oxide films.

When the frictional force is measured between an elastically restrained body and a driven surface, oscillations occur, as was observed by Kaidanovsky and Haykin (1933). Bowden and Leben (1940) refer to these as 'stick slips', and attributed them to actual welding of the asperities.

This suggestion of stick slips has resulted in a considerable controversy to which most workers on friction have now contributed. There is a general agreement that stick slips, as a form of relaxation oscillation, would arise given the necessary dynamic properties of the friction-measuring apparatus and the stipulated variation of friction force with sliding speed (see for example Haykin, Lissovsky and Solomonovich 1940, Blok 1940, Morgan, Muskat and Reed 1941, Bristow 1947). Schnurmann and Warlow-Davies (1942) have advanced evidence that the required force–velocity characteristic of sliding would arise from contact electrification. However, no one has yet correlated stick slips observed between a particular pair of materials with the appropriate measurements of the friction force over the velocity range. The concept of limited slip, however, suggests a mechanism whereby stick slips would arise. It is clear that, as the elastic member is deflected, the gradual rise in tangential force will give slip that is counteracted by a growth in the real areas of contact. The elastic member will thus move more slowly than the driven plate up to the point of macroslip. After macroslip the real area of contact is reduced to its initial value, and the phenomenon will be repeated to give a progressive stick slip process. This process incidentally explains the creep of the top slider noted by Bristow (1942). With this explanation there is no need to postulate welding which, after all, is a confusing way of describing intermolecular forces, the nature of which is still largely unknown.

The linear relationship between the force of adhesion and the tangential force of friction on the one hand, and between the real and apparent areas of contact on the other hand, confirms that both forces have a common origin in cohesion. The asperity theory is further disproved in the case of plastic deformation by the fact that these relationships, in so far as the tangential force is concerned, are not affected by the progressive increase in the degree and extent of scratching. These observations have been confined to lead and indium, but must be capable of wider application since even the asperities of hard materials are deformed plastically. Tabor (1949) has calculated that even the minute asperities of tool steel will be deformed beyond their elastic limit under the smallest practical loads.

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The Thermal Etching of Single Crystals of Cadmium

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ABSTRACT. The heating of single crystal wires of cadmium in circumstances that permit free evaporation produces a development of crystalline planes. When the basal plane makes a small angle with the axis of the wire there is a characteristic formation of hexagonal pits, the bottoms of which are mirror-like basal planes : when the basal planes make larger angles, characteristic elliptical traces appear, reminiscent of those formed by mechanical extension. The thermal etching reveals, by the formation of steps, thin laminae existing in the unstrained wire : the thickness of these, of the order of 1 μ, is the same as the spacing of the glide planes revealed by mechanical extension. The etched figures, in general, indicate that the substructure revealed by straining is already present in the unstrained crystal. The secondary pyramidal faces revealed agree with the calculations of Stranski, Kaischew and Krastanov.

The mirror-like basal planes are sufficiently large to permit the application of an optical method to reveal a scatter in their inclination to the axis. This method shows that there is a variation, round about 20 minutes, of orientation among the basal planes about the direction of growth of the crystals, which were grown by the method of Andrade and Roscoe and showed good single crystal properties by the usual criteria.

§1. INTRODUCTION

In the course of work which we have been carrying out on the effect of surface conditions on the mechanical behaviour of single crystals of cadmium, in the form of 1 mm. diameter wires, it seemed desirable to try to obtain the cleanest possible surface. No form of mechanical polishing is allowable, because the crystal structure of the soft wire is so easily deformed, and our investigations have shown that the contact of electrolytes has a marked effect on the mechanical properties (Andrade and Randall 1948), with the consequence that electrolytic polishing introduces factors not fully elucidated at the time when the work here described was undertaken. It was therefore decided to remove the surface layers of the wire by evaporation *in vacuo*.

In the first case the wire was heated by the passage of an electric current, being contained in a wide tube, the whole walls of which were comparatively cool: later the wire was heated in a wide tube in an electric furnace, from which the ends of the tube protruded. In both cases the effect proved to be not a general evaporation from the surface, but a number of local attacks, which showed interesting features. The heating by passage of a current, either D.C. or A.C., of a wire which had been kept as free from strain as possible resulted in a very marked preferential attack on certain selected glide planes, traces of some of which, but not all, were just visible with special illumination before heating, in spite of the very careful handling. The heating in a wide tube with cooled ends produced etch pits, the flat bottoms of which were hexagonal basal planes with a mirror-like surface. The walls of these pits showed a stepped structure, the 'treads' being close parallel planes, which were likewise hexagonal basal planes. The spacing of these planes was shown to be the same as that of the glide planes revealed by subsequently straining the same crystal. The 'risers' of the steps bounding the pits were $\{10\bar{1}1\}$ planes. The preferential development of the planes in question may be explained in a general way on the lines first indicated by Kossel (1927, 1928, 1930) and Stranski (1927, 1928, 1929, 1931, 1932).

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Single crystals of cadmium were also prepared from polycrystalline wire under conditions that permitted free evaporation during manufacture.

One important general conclusion which this work permits is that there exists in metal single crystals, as normally prepared, a substructure with spacing of the order 1 μ which is revealed, but not caused, by strain. This is a point which has already been discussed by Graf (1942), whose paper, published during the war, became accessible to us only after the experimental work was finished.

We have also been able to measure optically the angle between the crystal axes in the basal planes which bound lamellae and to show, as has been argued from x-ray measurements but not directly proved, that there is a scatter, of the order of 1°, in the direction of the axes pertaining to consecutive elements of the substructure.

The experiments here described concern cadmium only. However, thermal etching has revealed a similar substructure in the single crystals of gold and silver which Dr. Cyril Henderson has prepared in this laboratory. An account of the results with these face-centred cubic crystals will be published shortly. The method of thermal evaporation, which is another aspect of what is already known as thermal etching, appears to be a promising one for the investigation of the structure of the real metal single crystal, as distinct from the geometrical ideal.

§ 2. EXPERIMENTAL PROCEDURE

All the crystals used in the earlier part of the investigation were made by the Andrade–Roscoe travelling furnace method (Andrade and Roscoe 1937), in which the wire is enclosed in an evacuated tube whose internal diameter exceeds that of the wire by some 50 per cent. By this arrangement no constraint is imposed on the wire surface, but the curvature of the tube is sufficient to maintain the wire, which has been locally melted, in cylindrical form. No appreciable evaporation takes place, for while the temperature of the metal is near the melting point at the middle of the short furnace, and at room temperature outside the furnace, the solid angle subtended at the centre of the furnace by the space between cold wire and tube, where condensation might take place, is so small that the number of metal atoms travelling in straight lines that can escape from the heated part of the wire is negligible. This is confirmed by the fact that no observable condensation of metal on the walls of the cold part of the tube takes place.

The wires were sealed off in Pyrex tubes at a pressure of about 3×10^{-4} mm. Hg. Before the introduction of the wire the tube had been carefully cleaned and baked out under vacuum conditions at 400° c. and the technique adopted allowed the vacuum to be maintained during the transference of the wire to the clean tube.

(i) *Heating by Passage of Electric Current*

The single crystal wire was placed in the apparatus shown in Figure 1, the transfer being effected with the help of a cradle which was designed to keep the wire strain free. The wire was clamped to brass attachments at A and B; the ends lay in semi-cylindrical grooves in the brass, in which they were retained by small plates, also provided with semi-cylindrical grooves, held to the main attachment by screws. This method of fixing minimized chance strain. The holder A was attached to a terminal block at C, fastened to the brass box MNOP; B was attached by flexible coils of fine wire to E, which was carried by a vertical steel rod F, rigidly attached to the box MNOP. A current could thus be passed through the wire by terminals attached to C and to the box. The cylindrical prolongation of B passed through a hole in the plate D so that the wire could expand freely when heated by the passage of the current: after the current had been cut off, B could be clamped in position by a screw operated by the head H, which could subsequently be completely withdrawn. The object of this clamping was to avoid strain when the wire was being removed. The box MNOP had a removable glass front: the glass tube TTT fitted into a conical holder, from which it could be withdrawn. The arm SS was not involved in the experiments now under consideration. The wire was surrounded by the wide glass tube W; the metallic coating which formed on this tube indicated the amount of evaporation that had taken place.

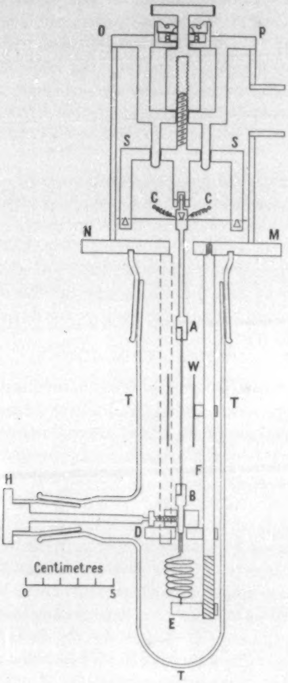

Figure 1.

Experiments were carried out in this apparatus with A.C. of about 4 amp. passing through the wire. A subsidiary experiment in which a 40 S.W.G. thermocouple was attached to the centre section of the wire indicated that the temperature in this region was about 250° C. The weight of metal deposited on the tube W, kindly determined for us by Mr. Tobe, indicated an average removal of about 30 mg/cm^2 from the surface of the wire, or, say, a layer about 4×10^{-3} cm. thick. After such thermal treatment the wire showed very markedly intersections of certain of the hexagonal planes with the surface of the wire. The general appearance of such an elliptical marking was reminiscent of the narrow segment that separates two glide packets in a crystal which has been considerably strained, but in the crystal subjected to thermal evaporation the bared portion of the hexagonal plane is considerable, and in consequence the trace shows a deep groove. Figure 2 (Plate I) represents a crystal (for which ψ, the angle made by the basal planes with the wire axis, is 70°) after it has been heated for 15 minutes at about 250° C. by the passage of A.C. This particular crystal had probably been slightly strained in handling or by the weight of the attachment B (Figure 1), which caused faint elliptical traces to appear, but even the faintest of those appearing in the photograph are much more marked than any of those visible before the surface evaporation.

In order to investigate further the development of the elliptical traces we selected a portion of a 25 cm. long crystal made in the normal way, which showed faint elliptical traces under special illumination. We never succeeded in making crystal wires 25 cm. long on parts of which very faint elliptical traces could not be seen, and can only suppose that, although the crystals that we prepare never adhere to the glass, nevertheless, during cooling and consequent shrinkage, the friction of the wire on the glass, which is very small, may be sufficient to produce a few very faint traces of slip bands in the hot wire.

The crystal, for which $\psi = 20°$, was extended by 1% to develop the glide planes slightly and then heated for an hour at 250° C. in an evacuated tube, the ends of which protruded from the furnace, so as to permit condensation. The effect on the traces is shown in Figures 3, 3(*a*), 4 and 4(*a*). At A in Figure 3 the very fine line shows the appearance of a slip band before etching. These and other undeveloped traces, which can also be seen in the photograph, require special illumination to make then visible: they are, however, more marked than the very faint traces in the unstrained wire, to which we have referred. In Figure 4 can be seen a developed trace made up of well-defined crystal planes, the broad line representing in a general way the intersection of a basal plane with the wire surface, and the lines AB and BC the development of either pyramidal or prismatic hexagonal faces. No such development has been seen to occur where a faint trace was not first visible with suitable illumination.

With the etching of tungsten (body-centred cubic) crystals, Schmidt (1947), following the work of Johnson (1938), found a difference in the effect of D.C. and A.C. heating, which he attributed to ion migration under the D.C. The effect of D.C. heating was therefore investigated. The general effect was, however, the same as that of A.C. In particular, no difference of effect could be found at the diametrically opposite sides of elliptical traces.

Besides the elliptical traces, representing bared hexagonal planes, many etch pits appeared on the surface. These are discussed in the next section.

(ii) *Furnace Heating*

To avoid, as far as possible, all strain of the crystals it was decided to make the single crystal and subsequently evaporate its surface without any intermediate transfer.

(*a*) *First method.* A Pyrex tube, whose bore exceeded the diameter of the wire by the usual 50% or so, was ground to form a trough of semicircular cross section and a cleaned wire placed in it. The trough was then set horizontally in an evacuated tube 1 cm. in internal diameter, and the small furnace made to travel along it as for normal single crystal manufacture, the difference from the normal case being that the metallic vapour was free to escape into the cool parts of the wide tube. During local melting and recrystallization the evaporation was, in fact, so heavy that the wire was much reduced in diameter. One long single crystal was not formed, but large grains occupying the full diameter of the wire, and some four diameters long, were produced. Such a single crystal grain is represented in Figure 5 (Plate II); it shows sets of facets about $100\,\mu$ across, traversed by parallel striations indicating lamellae about $1\,\mu$ across. Such lamellae are shown at higher magnification in Figure 6. Analysis of x-ray back-reflection photographs showed that such grains were single crystals with an orientation spread not exceeding 1°. The striations were traces of $\{0001\}$ planes, as indicated by comparing the results of optical and of x-ray measurements. Optically the reflections showed hexagonal symmetry as the wire was rotated about its axis: they proved to be due to $\{10\bar{1}2\}$ planes. These experiments revealed the existence, in single crystals formed by recrystallization of bulk material, of a lamellar structure similar to that found, for instance, by Straumanis (1931) for zinc crystals formed by condensation of vapour. They did not, however, give an unstrained crystal with cylindrical surface which could subsequently be thermally etched.

(*b*) *Second method.* To hinder evaporation the semi-cylindrical trough was surrounded by a close-fitting quill Pyrex tube as shown in Figure 7 and the whole

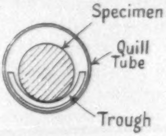

Figure 7.

exposed to the travelling furnace as before. Crystals formed in this way from polycrystalline wire showed, before evaporation treatment, neither facets nor developed elliptical traces. Prominent, however, were pits scattered at random on the surface and, in addition, certain grooves running round the wire in a plane normal to the axis. Surface evaporation was produced by heating the wire, which was protected from chance strain by never being taken from its cradle, at 250° c., for $\frac{1}{2}$–$\frac{3}{4}$ hour in an evacuated tube with ends protruding from the furnace. This resulted in an enhancement of the grooves and a development of the pits. The appearance of these grooves was quite independent of the crystal orientation with respect to the wire axis (see Figures 8 and 9 (Plate II), where the close parallel lines are traces of the $\{0001\}$ planes). They were in some cases traced to slight annular marks, visible on the wire as it comes from the drawers, and most probably were due to irregularities in the drawing process. If the intersection of these fine grooves with the wire surface gives edges of very small radius of curvature, then the excess vapour pressure given by the Kelvin equation may account for preferential evaporation in these regions. The grooves would appear to be trivial, and we have not followed the matter up.

The appearance of disconnected pits is characteristic of wires for which the basal planes made only a small angle with the wire axis, i.e. ψ small. When

ψ is 20° or greater, the characteristic development of traces of the basal planes, as exemplified in Figures 2, 3 and 4, takes place.

The etch pits presented different appearances according to their angular position as measured from a plane containing the wire axis and the normal to the hexagonal basal plane of the lattice. The two extremes are represented diagrammatically in Figure 10. In (*a*) the pit has formed in the neighbourhood of a normal to the basal plane through the wire axis and presents at the bottom a hexagonal plane which gives specular reflection. In (*b*) the pit has formed in the neighbourhood of a normal to the wire axis which lies in a hexagonal basal plane and shows a series of striations. Actual cases are shown by the photographs of Figures 11 and 12 (Plate II), which represent case (*a*), and Figure 13, which represents case (*b*). Should the {0001} plane AB, Figure 10 (*a*), make a large angle with the wire axis, the hexagonal plane in which the pit terminates may not be readily visible (Figure 14, Plate III) but becomes so when the wire is extended, with consequent rotation of the {0001} planes. Figure 15 shows the pit of Figure 14 after an extension of 250%. The mirror-like plane that terminates the pits was identified as an {0001} plane by x-ray back-reflection photographs. The bright lines in Figure 12 are given by reflection from the small portions of hexagonal basal planes which form steps in the sides of the pits, e.g. X in Figure 10. Similar reflections may be obtained from the small portions of planes Y in Figure 10 in pits with one or more incomplete sides. The angle between the hexagonal basal plane and the planes Y forming the sides of the pits was found by means of an optical goniometer to be 65°. This corresponds to the angle to be expected if the Y planes are $\{10\bar{1}1\}$ pyramidal planes, the directions of the edges of the bared hexagonal basal plane ensuring that the planes are $\{10\bar{1}k\}$.

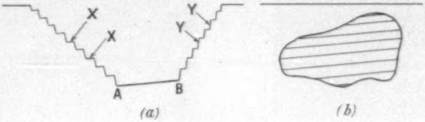

Figure 10.

It is clearly of interest to know if the laminae revealed by thermal etching correspond to those which appear as glide packets when the wire is strained. Observation under the microscope made it clear that there was a general correspondence, in so far as certain of the planes revealed by etching could be seen to develop further during strain. As a quantitative check the average thickness, normal to the basal plane, of some 100 lamellae was measured as they appeared after an extension of 5%: the figures in the two cases were $0{\cdot}75\,\mu$ and $0{\cdot}85\,\mu$ respectively, which, considering that a certain arbitrariness is introduced in determining whether certain faint marks are to be counted or not, is satisfactory. With large strains of 200% or so fresh slip bands appear, with a consequent diminution of average thickness of the laminae to about 4/5 of that indicated by the etch figures. Hence there appears little doubt that the defects of lattice which lead to the laminar appearance of the crystal where the surface has been removed by evaporation are the same defects that cause the glide packets revealed by strain.

(iii) *Lack of Parallelism of Packets*

The slabs of crystal lying between two consecutive 'preferred' planes, that is, planes revealed as privileged either by thermal etching or by the glide produced by stress, will be called a packet. Now if the preferred planes, or transition layers, as W. G. Burgers (1947) calls them, contain a set of parallel dislocation lines of the same sign (see Burgers 1947, Figure 4) there will be a small angle between the axes of successive packets, which will be evidenced by a lack of parallelism between consecutive basal planes revealed by thermal evaporation.

Experiments were therefore carried out to measure by optical reflection variations of angle between near planes revealed by thermal evaporation. The optical arrangement adopted is shown in Figure 16. The lamp filament A is focused on a 0·1 mm. vertical slit and an image of the slit, magnified 3 times, is formed, after reflection from the mirror surface E, on the front of the objective F of a microscope.

The objective is half covered by the stop G, the vertical edge of which is parallel to the image of the slit. The microscope is focused on the face of E. Rotation of E in an anti-clockwise direction causes the image of this face to disappear sharply when the image of the slit crosses the edge of the stop. If in place of the mirror E, used for test, a crystal with hexagonal planes exposed by etching be used, observation on the extinction of various facets constitutes a test for lack of parallelism.

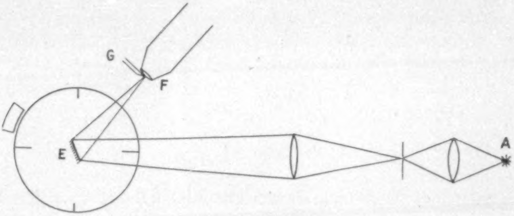

Figure 16.

The crystal was mounted on a goniometer (which allowed angles to be read to within 1′) with the portion under observation on the axis of rotation. It was prepared and transferred to the goniometer with great care, to reduce the possibility of chance strain to a minimum; the fact that the changes of angles did not progress systematically along the wire suggests that the wires were, in fact, undistorted. As a test, some measurements were carried out with a mirror surface on which all but certain strips, of about the same width as the exposed crystal faces, were rendered non-reflecting. These measurements showed that the method was satisfactory.

The hexagonal planes exposed by evaporation at the bottom of the pits gave sharp reflection and appeared, as far as these experiments can indicate, to be optically flat. Figure 17 (Plate III) shows a typical pit, and Figure 18 one corner under higher magnification. Owing to diffraction the steps at the side of the pit are never sharply defined.

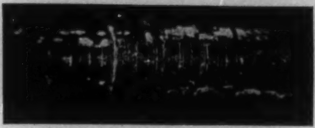

Figure 2. ×20. $\psi=70°$.
¼ hr. at 250° c.

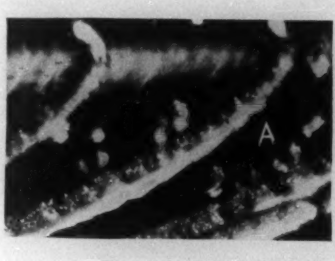

Figure 3. ×100. $\psi=20°$.
1 hr. at 250° c.

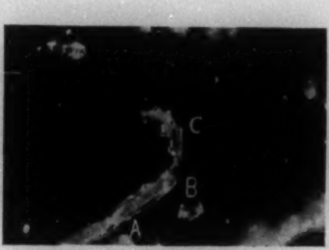

Figure 4. ×100. $\psi=20°$
1 hr. at 250° c.

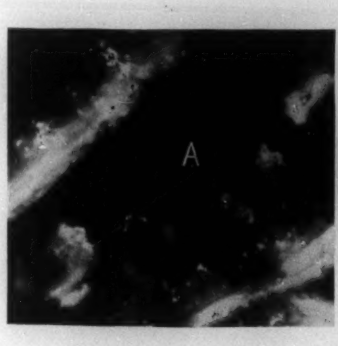

Figure 3 (*a*). ×300.

Figure 4 (*a*). ×300.

Thermally etched 1 mm. cadmium wires.

PLATE I.

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Figure 5. ×40.

Figure 6. ×600.

Crystal grain; $\psi=45^\circ$.

Figure 8. ×20.

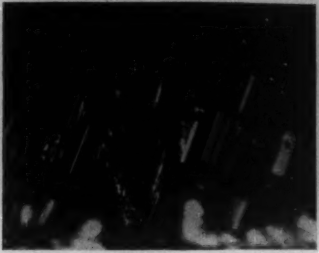


Figure 9. ×150.

$\psi=60^\circ$; showing annular marks.

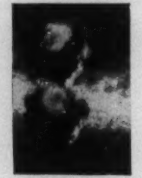


Figure 11. ×100. $\psi=4^\circ$.
See Figure 10 (*a*).

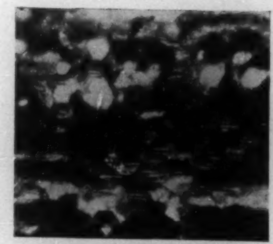


Figure 12. ×100. $\psi=2^\circ$.
See Figure 10 (*a*).

Figure 13. ×60. $\psi=10^\circ$
See Figure 10 (*b*).

Etch formations in 1 mm. cadmium wires.

PLATE II.

Figure 14. ×80. $\psi=30°$.
No extension.

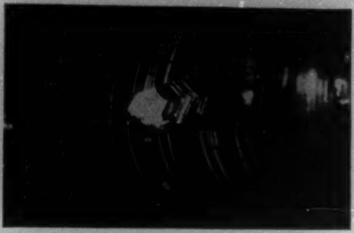


Figure 15. ×60.
As Figure 14, but $2\frac{1}{2}$× extension.

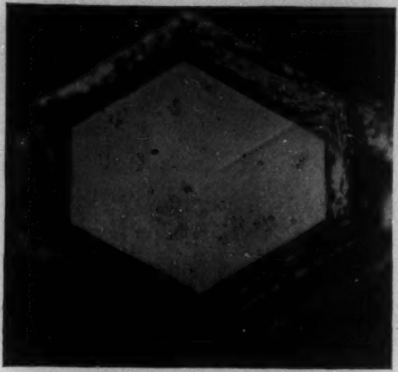


Figure 17. ×1,200. $\psi=4°$.

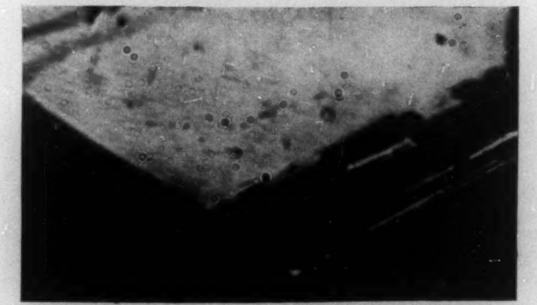
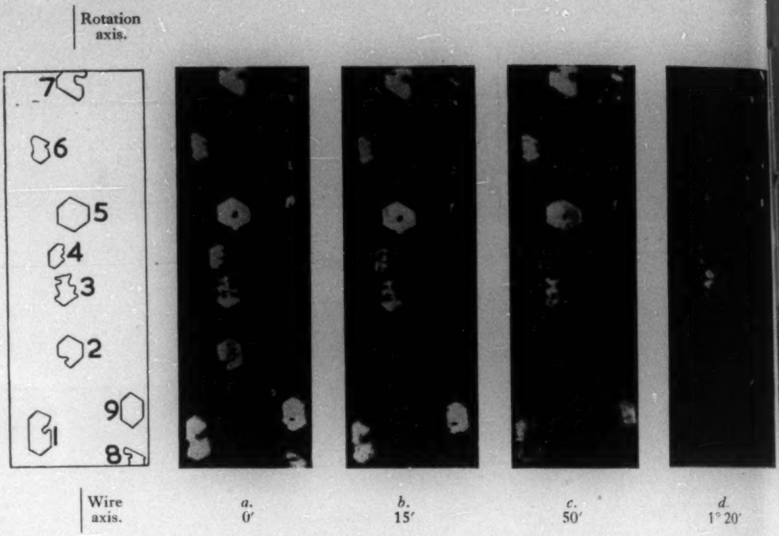


Figure 18. ×1,800. $\psi=4°$.

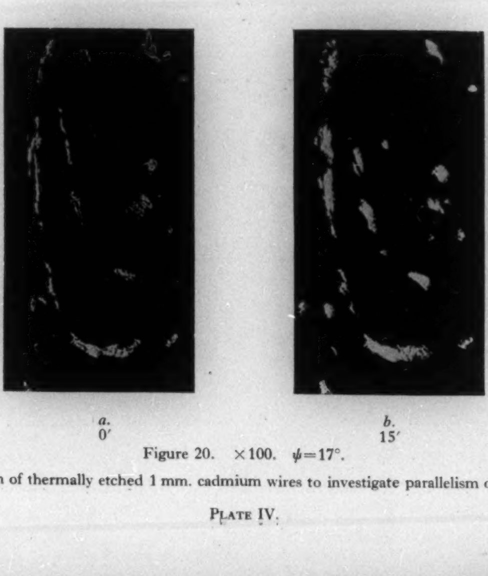
Etch pit formations in 1 mm. cadmium wires.

PLATE III.


Rotation axis.
7
6
5
4
3
2
9
1
8
Wire axis.

a. 0′ *b.* 15′ *c.* 50′ *d.* 1° 20′

Figure 19. ×70. $\psi=4°$.



a. 0′ *b.* 15′

Figure 20. ×100. $\psi=17°$.

Rotation of thermally etched 1 mm. cadmium wires to investigate parallelism of facets.

PLATE IV.

With a wire for which the angle ψ made by the hexagonal planes with the wire axis was 4°, mounted with the wire axis vertical (position 1), the appearance of a typical group of pits is shown in Figure 19(*a*), Plate IV. Figures 19(*b*), (*c*) and (*d*) were taken after rotations from (*a*) of 15′, 50′ and 1° 20′ respectively. In (*b*) pits 2 and 8 have already disappeared; in (*c*), in addition, 1, 4 and 9 are going; in (*d*) all have vanished except a part of 3. In all cases the edges remain after the corresponding main reflection plane has gone, probably owing to diffraction. In estimating the angle at which extinctions took place allowance was made for difference of position with respect to the axis of rotation. In the case of visual observations it was found that the position of extinction of a given facet could be reset to better than ± 5′. In the case of photographic treatment the pictures were taken at about 15′ intervals.

Figure 20 shows another crystal, with $\psi = 17°$, in two positions differing by 15′. It will be seen that in (*b*) a crystal surface just below the mid-point has disappeared, and close examination will reveal other differences.

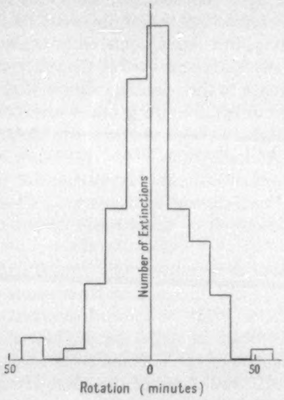


Figure 21.

Six crystal wires were tested with the surfaces of the basal planes on or near the axis of rotation and the wire axis in the same vertical plane as the axis of rotation. Further, one of the crystals was tested with the wire axis normal to the axis of rotation so as to test for lack of parallelism in the direction of growth. In this position eighteen planes were measured optically and no difference of angle greater than 5′ could be detected.

For the six crystals investigated with the axis of rotation near the wire axis the variation in angle between the facets was determined relative to an arbitrary mean value. This gave in all 113 deviations from the mean, for which a frequency histogram is plotted in Figure 21. The mean deviation is 18′, which expresses the lack of parallelism.

Our conclusion thus is that, as regards potential glide planes, there is a probable variation of angle about the direction of growth (projection of wire axis on glide planes) of about $\pm 20'$. On the other hand, there is no variation of angle within the limit of accuracy of our observations (about $\pm 5'$) about a line at right angles to the direction of growth.

It should be emphasized that these results are presented as preliminary, the normal distance between the planes concerned not having been measured, and the number of measurements not being sufficient for a proper statistical handling. The results suffice, however, to illustrate the method.

§ 3. DISCUSSION

The phenomenon of thermal etching in single crystals has been observed with tungsten filaments by Johnson (1938) and by Smithells (1936) who has drawn attention to the structural features revealed by the differential rates of evaporation from different crystal faces. Smithells has published photographs showing the development of large hexagonal surfaces and of planes very regularly spaced at distances of the order of $1\,\mu$. Johnson also records the exposure of smooth $\{100\}$ faces by evaporation and several interesting observations on the surface migration of ions with D.C. heating, but failed, apparently under the conditions of his experiments, to reveal any block structure of the order of $1\,\mu$. Neither of these authors make any reference to the possible relation of these surfaces exposed by evaporation to the surfaces bared by glide under mechanical forces. Which are the glide planes of tungsten at high temperatures does not seem to have been determined, but from Andrade and Chow (1940) they would be anticipated to be $\{123\}$. Smithells does not state the designations of the close planes revealed in his photographs. In discussing block structure, Graf (1942) describes the systems of parallel markings left on the surfaces of cast metals which have been carefully cooled.

The structure of small cadmium crystals formed from the melt or from the vapour has been described and discussed by Straumanis and by Stranski and his collaborators. Straumanis (1931) has shown that crystals of hexagonal plates, of thickness about $1\,\mu$, laid down in steps, the surfaces of the steps being $\{0001\}$ planes. The most frequent of the inclined faces were $\{20\bar{2}5\}$ followed closely by $\{10\bar{1}2\}$ and $\{20\bar{2}3\}$. He also observed the effect of vaporization on the small crystals of a deposit formed on a glass rod, and likewise observed the baring of $\{0001\}$ surfaces. He produced glide lamellae in a small zinc crystal about 1 mm. high and less in diameter by pushing it with the point of a needle, and found a thickness of $0{\cdot}8\,\mu$ (1932).

Except, then, for the work on tungsten single crystals, there do not appear to be any observations on the effect of evaporation on single crystals, and all that was clearly established with tungsten was the existence of steps due to the baring of unspecified planes which were separated by, as far as can be judged by the photographs, about $1\,\mu$.

The first thing that is clear from the present observations is that on the surface of a single crystal, prepared as carefully as possible and never removed from its cradle, there are spots of high free energy, where the vapour pressure is abnormally high. From these, pits form which show the preferential development of the basal planes and the secondary pyramidal faces explained by Kossel and Stranski on considerations of the number of near neighbours of different classes among the ordered atoms. The pyramidal faces found by us from a consideration of x-ray and optical methods were $\{10\bar{1}1\}$, which agrees with the calculations of Stranski, Kaischew and Krastanov (1934) for the close-packed hexagonal lattice from which cadmium deviates but little.

If the basal plane makes a very small angle with the wire axis the etch pits appear to form in lines parallel to the wire axis. This may be due to drawing marks which are still visible after the crystal has been made. High vapour pressure at the sharply curved edges of the marks would then initiate evaporation. When the basal planes are nearly parallel to the wire axis, all directions in the surface through a given point are nearly equally favoured as regards removal, and there seems to be no reason why a pit should develop in one direction rather than another, which accounts for the symmetry of the pits about a centre. When ψ is larger the line of intersection of the basal plane with the surface is, of course, in the basal plane, while the normals to this line which lie in the surface make a considerable angle with the basal planes. Hence removal is easier along the line of intersection than along a normal to the surface, which accounts for the development of the 'glide surfaces'.

For larger angles the etch pits tend to extend along the intersection of one particular basal plane and give rise to elliptical traces. An intermediate effect is shown in Figure 4, where the attack has bared pyramidal faces and so led to a hexagonal outline.

All our experiments show the basal planes as the most stable. The evaporation of prepared crystals showed $\{10\bar{1}1\}$ to be the most stable pyramidal plane, in agreement with Stranski, Kaischew and Krastanov. In the case of the crystal evaporated during preparation the $\{10\bar{1}2\}$ planes appeared. The various pyramidal planes have nearly the same binding energy and have all been detected by different observers with cadmium crystals prepared by different methods.

The spacing of the $\{0001\}$ planes is of the order $1\,\mu$, and this is in accordance with the observations of Graf and appears to be the unit of the fundamental secondary structure.

Thus a significant conclusion to be drawn from the work is that the glide planes are apparently no more than developments of a structure already present in the crystal. Photographic observation of the extension of an etched crystal may be expected to confirm the identity of the etch lines and glide planes.

The variation of orientation recorded between different glide planes is almost certainly about the direction of growth and not about the digonal axes, as there are three of these and there is no apparent reason why any one should take preference over the other two. So far shear has always been near the direction of growth, and experiments in which this is not so should distinguish between the digonal axes and the direction of growth as directions about which the departure from parallelism occurs.

The method of thermal etching thus has considerable potentialities in the investigation of the secondary structure of single crystals, and should be able to show conclusively that the occurrence of preferential glide on certain selected planes is dependent on a structure already present.

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The Lattice-Parameters of Clear Crystalline Quartz

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ABSTRACT. Some experimental results are presented showing that the calibration of Debye–Scherrer x-ray diffraction cameras by means of clear crystalline quartz may lead to appreciable errors unless the parameters of the quartz are first determined by a direct method. The parameters of a sample of clear Brazilian quartz have been found to be in serious disagreement with the accepted values, and variations in the parameters of synthetic quartz, with an apparent dependence on growth temperature, have also been observed. Taken in conjunction with previous results of other workers, the experiments show that quartz parameters vary from sample to sample by amounts as large as 0·01% according to the impurity content. The previously proposed quartz calibration standard is rejected.

§ 1. INTRODUCTION

The investigations to be described were carried out with a 'Unicam' cylindrical x-ray powder camera of 19 cm. diameter. With a camera of this type it is desirable to calibrate the fiduciary knife-edges directly, but an alternative method has been widely used in which standard values of the quartz parameters are employed to determine the camera angle by extrapolation (Bradley and Jay 1933, Lipson and Wilson 1941a). In some focusing cameras a direct calibration is either impossible or extremely difficult, and a secondary standard must then be employed.

For the standard Bragg angles of quartz, Bradley and Jay suggested those calculated from Bergqvist's value of the *a*-parameter and the assumed value, 1·10002, for the axial ratio at 18° c. Using a camera of 9 cm. diameter, they showed that this value was an improvement on an earlier figure due to Groth. Both the *a* and *c* parameters were redetermined with another sample of quartz by Lipson and Wilson (1941a), and these authors ensured a much higher accuracy by making a large number of measurements with three different characteristic radiations.

Their parameters, obtained with a 19 cm. camera, are approximately 0·007% larger than those of Bradley and Jay. In revising the quartz standard, however, Lipson and Wilson apparently studied one sample of quartz only, possibly relying on the fact that Bradley and Jay had previously found no significant differences in the parameters of two samples of clear quartz of different origin. In view of the method adopted by Bradley and Jay, and the fact that they used only two samples, it is difficult to avoid the conclusion that they did not adequately establish the invariability of the parameters of clear crystalline quartz of different origins.

Both the quartz and the direct methods were employed for the calibration of the camera used in our investigations, and good agreement was found between the directly determined camera angle and that obtained from quartz angle extrapolations if the quartz Bragg angles of Bradley and Jay were employed. When the angles given by Lipson and Wilson were used, however, the agreement was not as satisfactory, a result which had previously been observed in this laboratory by Mr. P. Vousden when he calibrated a separate, but similar, camera. In all these calibrations the specimens were prepared from clear Brazilian quartz derived from the same large single crystal. On account of the agreement between these independent observations and of the importance of accurate camera calibration, the parameters of this quartz were determined directly. The relative accuracy of the parameter measurements is of the order of 1 part in 10^5, and their absolute accuracy must approach this very closely.

§ 2. DISCUSSION OF THE EXPERIMENTAL TECHNIQUE

(*a*) *Direct Calibration of the Camera*

Two methods described by Lipson and Wilson (1914 a) were employed for the direct calibration. With a spectrometer table of large radius the camera angle was found to be 85·299°; by measuring the radius of the camera and the chord width of the knife-edges it was calculated to be 85·300°. The goniometrical method is more reliable and eight independent measurements of each knife-edge were made, giving a spread of 0·0065° in the camera angle and a probable error of ±0·002°. In all the later determinations of the parameters of quartz the value $\theta_k = 85{\cdot}299°$ has been used.

(*b*) *Temperature Control*

To provide the necessary constant temperature conditions for the experiments, an air thermostat was built which would house the entire camera assembly, and this maintained the temperature constant to within ±0·2° c. for many days. This method is valid, however, only if the specimen is not heated appreciably by the x-ray beam during the exposure. Both energy calculations and confirmatory experiments show that this does not happen.

(*c*) *Discussion of the Inherent Errors*

The geometrical and absorption errors in non-focusing powder cameras can be eliminated readily by extrapolation (Bradley and Jay 1932, Lipson and Wilson 1941 b, Taylor and Sinclair 1945, Nelson and Riley 1945), and the limit of accuracy which can be attained is determined almost entirely by the reliability of the film measurements. Insufficient attention has been paid to the accuracy limits imposed by visual setting errors, and consideration of these factors has led us to modify the existing technique in the following respects. We prefer (i) higher microscope magnifications, and (ii) somewhat thinner specimens than have previously been considered profitable.

With regard to (i) above, Lipson and Wilson recommended a microscope magnification of 3 diameters for all the film measurements, but we consider that a larger magnification is advantageous. At 3 diameters it is difficult for an observer to distinguish with ease and certainty the true density maximum of a diffraction line even though his settings may have a good reproducibility. Errors may also be encountered in setting on the knife-edge shadows where there is a marked contrast in brightness between the two halves of the field of view. Such errors were, in fact, found in some of our early experiments, and were investigated in the following way.

A scratch made with a razor-blade or a fine diffraction line in the neighbourhood of $\theta=45^\circ$ was taken on the film and the distance separating it from a knife-edge shadow measured. The film was then reversed in direction and this distance re-measured. Any discrepancy in the two results suggests an asymmetry in the illumination which should be avoided. Reliable settings can be obtained if the contrast at the edge of the shadow is reduced by placing parallel to it a sharp straight edge leaving only a very narrow slit of bright illumination. The difference between the length of the film as measured with and without this contrast reduction is the sum of the errors at the two edges in a typical film measurement. With a magnification of 3 diameters the magnitude of these errors is roughly a length of 0·002 cm. on the film at each edge, corresponding to 0·002% in the measured parameters. If higher magnifications are used, this source of error is no longer important since it then represents a correspondingly shorter length on the film.

It is important to use high magnification in the direct calibration of the knife-edges (§ 2 (*a*)) because a deviation of 0·002 cm. in the measured position of each edge corresponds to a change of 0·0065° in camera angle. This produces, in turn, errors of approximately 0·0025% in all subsequently measured parameters and also a tendency to curvature in the extrapolation plots.

All the film measurements on which our parameters are based have been made with a Cambridge Universal Measuring Machine, using 3 diameters magnification in some cases and 15 diameters in others. The Bragg angles measured with different magnifications on the same film are in good agreement, allowing for experimental error, but the spread in the experimental values is significantly less in the case of the higher magnification.

Consider now (ii) above. Very thin specimens have been used for the precision parameter determinations because of the consequent reduction in the breadth of the diffraction lines, which allows more precise measurements to be made. The spread of the experimental points on an extrapolation plot is thereby diminished, and the number of parameter determinations necessary to establish a given precision in the averaged result is reduced. This lowers the required number of laborious least squares calculations (see § 2 (*d*)), and the slightly increased exposure times required are no serious disadvantage. In all these experiments the specimens used were between 0·2 mm. and 0·3 mm. in diameter compared with diameters ranging from 0·5 mm. and 1·5 mm. used by previous workers.

The dependence on line breadth of the accuracy of each parameter measured was established by the following argument. Rymer and Butler (1945) showed that the standard deviation σ of visual settings on a broad diffraction line is closely proportional to the square root of its half-intensity breadth B. The relative error of setting r can thus be written in terms of B as

$$r = \text{const. } \sigma/B = \text{const. } B^{-\frac{1}{2}}. \qquad \ldots\ldots(1)$$

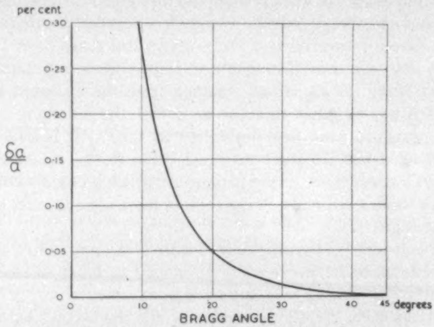
Inserting this into the equation

$$|\delta a/a| = |(rB/2R)\cot\theta|, \qquad \ldots\ldots(2)$$

given by Ekstein and Siegel (1949), for the corresponding error in the parameter we obtain the result

$$|\delta a/a| = \text{const. } B^{\frac{1}{2}}. \qquad \ldots\ldots(3)$$

If an extrapolation involving reflections over a wide range of Bragg angles is to be used care must be taken to keep μr, the product of the linear absorption coefficient and radius of the specimen, greater than 1·0 since otherwise the appropriate extrapolation against $\frac{1}{2}(\cos^2\theta/\theta + \cos^2\theta/\sin\theta)$ will not be completely linear. When a least squares calculation is employed with such an extrapolation, using Nelson and Riley's table of this trigonometrical function, it is advisable to correct the points corresponding to Bragg angles less than 45° for the geometrical error due to the finite length of the specimen irradiated (Bradley and Jay 1932, Lipson and Wilson 1941 b). The author has re-calculated the magnitude of this error and obtains a focusing term $\{1 + (R/AX)\cos 2\theta\}^2$ in place of that given by Lipson and Wilson. The relative error in parameter as a function of θ for values less than 45°, calculated from the assumption that $R = 95$ mm. and $AX = 150$ mm. and from the vertical slit lengths given by Bradley, Lipson and Petch (1941), is plotted in the Figure; the use of this will allow the necessary reduction in the parameters to be readily made. Although extremely fine lines could be obtained with vertical x-ray tube foci, this error prevents their use for these experiments since little focusing is then present in the vertical plane and the elimination of the error by extrapolation would be too troublesome.



Relative error $\delta a/a$ in parameter as a function of Bragg angle.

(*d*) *Extrapolations*

Graphical extrapolation methods can only be applied directly to the simplest structures, and even then do not readily allow the attainment of the high accuracy of which the powder method is capable. Favourable conditions for deciding the best line through the experimental points are usually incompatible with the use of a large scale of ordinates to give high accuracy in reading the extrapolated result. The method of least squares for calculating the most probable result from the experimental points (Cohen 1935) is equally applicable to any structure. It suffers, however, from one serious disadvantage in that it does not, of itself, make any allowance for widely scattered experimental values due either to computational mistakes or to setting errors. This is done automatically by inspection on a graphical plot. The difficulty can be obviated in the case of cubic structures by drawing a rough plot and assigning weights to the points according to their agreement with the extrapolation line. For more complicated structures, such as quartz, alternative methods can be employed.

In our experiments each powder photograph for a given specimen was measured several times and the Bragg angles averaged. Several photographs of each specimen were taken, measured and the average also taken over these results. This procedure has been used throughout to reduce the computational labour.

Before normalizing the equations obtained from the accepted values of the Bragg angles each was weighted in accordance with the following criteria:

(i) All the equations were first multiplied by $\tan\theta$. It is important not to omit this since otherwise we attribute equal value to the measurements at all Bragg angles. The sensitivity of the parameters given by $\delta a/a = \cot\theta\,\delta\theta$ is such, however, that a specified error in a Bragg angle is more serious in its consequences the smaller that angle.

(ii) Further subsidiary weighting factors were then applied to a small number of the equations to allow for the inevitably reduced accuracy of measurement in the case of fainter lines and of overlapping lines.

The parameters were calculated separately for the α_1 and α_2 lines and the results averaged with the respective weights of 2 and 1. The results of these separate calculations were in agreement to slightly better than 1 part in 10^5 except in the case of one synthetic sample where agreement to 1 part in 8×10^4 only was obtained. Finally, a correction was applied for the refractive index of the quartz.

§ 3. EXPERIMENTAL RESULTS

All the powder photographs were taken at 25° c. with copper radiation from the horizontal focus (8 mm. × 1 mm.) of a Metropolitan Vickers 'Raymax' x-ray unit. Four samples of clear quartz were studied: (i) the Brazilian quartz previously referred to, and (ii) three samples of unseeded crystals of synthetic quartz grown by the hydrothermal method (Hale 1948) at temperatures of 290° c., 380° c. and 390° c. In all cases sharp high-angle lines were obtained; the constancy of the parameters throughout the whole of the Brazilian crystal and one of the synthetic samples was established by studying several different specimens made from each. After averaging the Bragg angles in the manner previously described, the equations arising from seventeen lines with θ greater than 60° were weighted and a least squares calculation performed assuming the extrapolation to be linear in $\cos^2\theta$.

In order to facilitate direct comparisons with earlier results, we have deliberately used Siegbahn's values for the X-ray wavelengths, i.e. Cu Kα_1, 1·537395 kx.; Cu Kα_2, 1·541232 kx. The parameters found at 25° c. were corrected to their values at 18° c., the reference temperature used by previous authors, and the coefficients of linear thermal expansion given by Jay (1933) were employed for this purpose.

Lattice-Parameters (in kx.)

Sample	25° c.			18° c.		
	a	*c*	*c/a*	*a*	*c*	*c/a*
Brazilian quartz	$4\cdot90309_3$	$5\cdot39367_3$	1·100057	$4\cdot90258_5$	$5\cdot39333_3$	1·10010
Synthetic quartz (290° c.)	$4\cdot90372_8$	$5\cdot39415_8$	1·100012	$4\cdot90321_9$	$5\cdot39381_8$	1·100056
Synthetic quartz (380° c.)	$4\cdot90334_7$	$5\cdot39387_0$	1·100038	$4\cdot90283_9$	$5\cdot39353_0$	1·100083
Synthetic quartz (390° c.)	$4\cdot90324_8$	$5\cdot39384_4$	1·100056	$4\cdot90273_5$	$5\cdot39350_0$	1·10010
Bradley and Jay (1933)				4·90288	5·39327	1·10002
Same (modified by Cohen)				4·90287	5·39344	1·100057
Lipson and Wilson (1941)				4·90320	5·39371	1·10004

The second set of values given under the names of Bradley and Jay are those determined from their experimental Bragg angles by Cohen (1935) by means of a least squares calculation. Miller and DuMond (1940) also measured the parameters of a sample of natural quartz and obtained values considerably below ours and, therefore, diverging even further from Lipson and Wilson's values. They used a focusing camera which had been calibrated by a direct method. When expressed in kx. at 18° c. their parameters are $a = 4\cdot90220_9$; $c = 5\cdot39330_0$; $c/a = 1\cdot10018$.

§ 4. DISCUSSION OF THE EXPERIMENTAL RESULTS

It is immediately obvious from the results that the parameters of quartz are not sufficiently constant to found a precise standard upon them. The overall variations in parameters so far measured with 19 cm. cameras is seen to be 0·011%, while the experimental error is at most 0·0015% in the results of the different observers. Bradley and Jay (1933) demonstrated that the impurities in smoky, rose and milky quartz crystals caused relatively large increments in the parameters. Their experiments on different clear samples could not, however, be regarded as final; they assumed that the same axial ratio, for which their value is now known to be too small, held for all the specimens and employed rather inadequate graphical extrapolations throughout. The weakness of such a procedure has already been indicated by the calculations of Cohen. The variations found may possibly be interpreted as being due either to impurities or to holes built into the lattice during growth, but nothing is known of the existence or characteristics of such effects in the crystals used.

It is rather remarkable that in the parameters at 18° C. which we have calculated the axial ratio varies quite markedly and decreases as the parameters increase. The elastic anisotropy of quartz suggests that if impurities are present and cause a small stress in the lattice which is approximately homogeneous, then such a behaviour of the axial ratio can be explained. To test this further the results for the four measured samples were taken in pairs and the fractional increment in each parameter for a given pair determined. The ratio of these increments was then compared with the known ratio of the strain components, $s_{11}=1{\cdot}269\times10^{-12}$ and $s_{33}=0{\cdot}971\times10^{-12}\,\mathrm{cm}^{-2}\,\mathrm{dyne}^{-1}$, parallel and normal to the optic axis (Cady 1946). The ratio of the increments normal to the optic axis to those along that axis should therefore be $1{\cdot}269/0{\cdot}971=1{\cdot}307$ if the lattice is stressed isotropically. The experimental values were calculated and the six possible pairs of parameters gave 1·419, 1·438, 3·85, 1·675, 0·98, 1·453 for the ratio. The value 3·85 arises from a pair of parameters different from one another only by the order of the experimental error, and if it is neglected the mean ratio is 1·393. This agrees to within 10% with the theoretical value for homogeneous stress and, bearing in mind that these ratios are those of the increments in the fifth significant figure, this agreement is very striking. We may conclude that the results obtained may be interpreted as indicating that an impurity content in quartz produces a small stress in the lattice and consequent alterations in the parameters.

The apparent dependence of the parameters of the synthetic samples on growth temperature may be fortuitous; it is hoped to obtain further results later. The results for these crystals when plotted against the growth temperature lie on smooth curves.

ACKNOWLEDGMENTS

The author wishes to thank Dr. Danforth R. Hale, of the Brush Development Co., Cleveland, Ohio, for the samples of synthetic quartz used in the experiments. They were grown under contract from the U.S. Signal Corps. He is indebted to Dr. J. W. Mitchell and Dr. H. F. Kay for encouragement throughout the work, and also to the former for his assistance in the preparation of this paper. Finally, thanks are due to the Queen's University of Belfast and the Northern Ireland Ministry of Education for financial assistance.

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LETTERS TO THE EDITOR

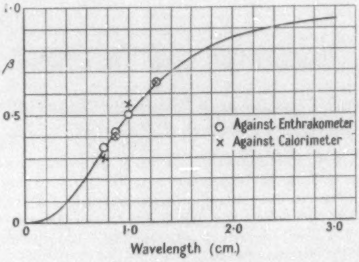
Discrepancies in the Measurement of Microwave Power at Wavelengths below 3 cm.

Recent experiments have shown that measurements of power at millimetre wavelengths, using a thermistor, may be in error by as much as 100% or more.

It has been the common practice at centimetre wavelengths to employ a water calorimeter for the measurement of high-level power (of the order of one watt or more). For low-level power, instruments have been used in which the power is absorbed in some form of resistance, the change in resistance being taken as a measure of the power. Instruments of this type are the bolometer, using a thin wire, the thermistor, using a semiconducting bead, and the enthrakometer (Collard 1946) using a resistive film.

At millimetre wavelengths the thermistor has been much employed, owing to its sensitivity and simplicity in use. Results obtained have been considered moderately reliable until recent experiments by one of us (J.C.) indicated a large discrepancy at a wavelength of 9 mm. between thermistor and enthrakometer measurements.

A water calorimeter, designed and constructed by G. Dalton of Telecommunications Research Establishment for the 7 to 12 mm. wavelength range and capable of measuring power levels as low as 20 mw. has made possible a direct comparison with the thermistor and enthrakometer. This comparison was carried out at T.R.E. over a wavelength range from $7\frac{1}{2}$ to $12\frac{1}{2}$ mm. at a power level of 20 mw. More accurate measurements were also made at 9 mm. of the enthrakometer against the thermistor for a power level of 1 mw. and of the enthrakometer against the calorimeter for 50 mw.; these measurements were consistent with the direct comparison of all three instruments. The source of power was provided by a range of reflection klystrons covering this wavelength band, made at T.R.E. and based on the original design of the Clarendon Laboratory, Oxford. The enthrakometer and water calorimeter agreed to within a few per cent, but the thermistor showed differences of the order of 100% as shown in the Figure.



Thermistor reading as fraction of actual power.

If the thermistor is considered as having a bead resistance R, shunted by a capacitance C, this combination being in series with the lead resistance r, it can be shown that the ratio β of the power dissipated in the bead to the total power is $\beta = 1/(1+\omega^2C^2Rr)$ provided $\omega^2C^2R^2 \gg 1$.

The effect of the capacitance C is to make the effective resistance of the bead very much smaller than R so that the lead resistance r becomes comparable to it.

Owing to the skin effect in the leads, the resistance r is proportional to $\sqrt{f}$. Assuming C and R independent of frequency we may therefore write $\beta = 1/(1+kf^{2\cdot5})$, where k is a constant for the bead.

An equation of this form has been fitted to the experimental points in the Figure. The agreement with the curve is good and requires $C\sqrt{(Rr)}=5{\cdot}3$ pF Ω at a wavelength of 1 cm. An estimate of r (for 0·001 in. diameter 70% platinum—30% iridium wire, approximately 0·04 in. long) is about 2·5 Ω at room temperature. The capacitance of a similar thermistor bead measured for us by the G.E.C. Research Laboratories, with a 45 Mc/s. bridge, was 0·2 pF. Assuming $R=150\,\Omega$, which is the D.C. operating resistance of the bead, we obtain $C\sqrt{(Rr)}=3{\cdot}9$ pF Ω, which is the right order of magnitude.

From the above equation it is expected that β will decrease with increase in R. Altering the D.C. resistance of the bead over a range of 150 to 600 Ω (by controlling the bias current through the bead) produced a much smaller variation of β than would be expected if R were proportional to the D.C. resistance. This may indicate that the effective value for R for the radio-frequency power does not vary as rapidly with temperature as the D.C. resistance. If the thermistor bead is a polycrystalline material, the D.C. resistance will probably consist of the contact resistance of individual crystals. Hence at high frequencies these resistances will be shunted by the contact capacities and the specific resistance of the material will tend towards that of the individual crystals. In addition, minor effects may be produced by the variation of lead resistances and a possible variation of capacitance with bias current.

From the Figure it is evident that power measurements by a thermistor can be in error by a large factor at millimetre wavelengths. At 10 mm., for instance, the power measured by the thermistor is about one half the true value. Of course, a thermistor can still be used if it is calibrated and, since there are indications that thermistor beads of a particular type give fairly consistent measurements, it may be possible to dispense with individual calibration and use instead a simple correction factor.

Acknowledgment is made to the Chief Scientist, Ministry of Supply, the Director of Radio Research, Department of Scientific and Industrial Research and to the Controller of His Majesty's Stationery Office for permission to publish this note.

E.M.I. Research Laboratories Ltd.,
Hayes, Middlesex.
J. Collard.

Telecommunications Research Establishment,
Ministry of Supply.
G. R. Nicoll.
A. W. Lines.

24th January 1950.

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REVIEWS OF BOOKS

Pulses and Transients in Communication Circuits, by Colin Cherry. Pp. xvi + 317. 1st Edition. (London: Chapman & Hall, 1949.) 32*s*.

This book, which is an introduction to the study of transients in networks, has been written with the object of bridging the gap between elementary A.C. theory and the methods of operational analysis, and in this the author has succeeded.

The scope is much wider than the title suggests, and there is little that cannot be profitably studied by anyone concerned with electrical communication, whether he is particularly interested in transients or not.

Among the topics discussed are the frequency spectra of various types of continuous and transient waves, Fourier series in real and complex form, conjugate vectors, Fourier integrals, equivalent and dual networks, the low-pass/band-pass analogy, the relations between the steady-state and transient response of a network, idealized networks, multi-stage amplifiers, echo effects in lines and networks, the method of paired echoes, and an introduction to transversal filters. In what is perhaps the best chapter of the book there is a thorough treatment of asymmetric sideband channels.

The author's method is " to use wherever possible rigorous physical arguments and only elementary mathematics. Mathematical language and notation are avoided as much as possible ".

In fact, however, elementary mathematics and notation are freely used, and there are few pages that do not have a formula or so. The reader may sometimes wonder how rigorous the arguments are, but happily the results are usually correct.

It is clear that the book is full of important material, and it is therefore most unfortunate that this otherwise excellent work should be marred by a large number of errors. Some of these are obvious, but others require some research on the reader's part.

The definitions of the impedance and transfer characteristics on p. 85 are very strange; for example, the output impedance of a network is apparently equal to any impedance which the reader cares to connect across the output terminals.

Section 36—" Example of Fourier integral analysis of circuit response "—should be disregarded; only the final answer is correct.

The author does not appear to have made up his mind whether the " infinitesimal pulse " whch he uses is a pulse of fixed amplitude and vanishingly small duration or whether it is of the Dirac type with a finite amplitude–time integral. The results obtained indicate the latter, but no clear definition is given and the two ideas are mixed in a bewildering fashion.

Section 47 deals with the suppression of the response which occurs in idealized filters before the signal is applied. The reader should ignore this Section. Both the method and results are wrong.

Distortionless and lossless lines are confused in Section 72. None of the formulae on pages 282–283 are valid for distortionless lines; some are true for lossless lines, others are simply not true.

These are only a few of the author's lapses. The list could be multiplied, but enough has been said to show that the reader, particularly if he is a beginner, will encounter several obstacles. It is difficult to avoid the conclusion that this book was written in a hurry, and it is to be hoped that the author will find time to make a thorough revision of both text and diagrams before a second edition is required. A. S. GLADWIN.

Viscometry, by A. C. MERRINGTON. 1st Edition. Pp. viii + 142. (London: Edward Arnold & Co., 1949.) 16*s*.

This slim volume is intended for the practical research worker, being a concise yet up-to-date account of most of the methods available for measuring viscosity. The minimum of theoretical detail is given, but otherwise the layout closely follows that of Barr's *Monograph of Viscometry*. The generous bibliography given at the end of each chapter should prove adequate even for the specialist in any branch of the subject. The inclusion of apparatus dimensions in the appendix is welcomed, but it is hard to justify the inclusion of a table giving the viscosities of sugar solutions of various cencentrations when, as the author points out, such a solution is not now recommended as a primary standard. C. D.

Physics: *Principles and Applications*, by H. MARGENAU, W. W. WATSON and C. G. MONTGOMERY. Pp. x + 760. (New York: McGraw-Hill Book Co., 1949.) 30*s*.

According to the authors this book is written for American second year University students in engineering and the major sciences. In England, the book may be found useful to some entrance scholarship candidates and first year post-intermediate students. The book covers ground which is mainly not new, and perhaps an attempt to cover too wide a field has been made. At times very elementary subjects are discussed and then, rather suddenly, difficult topics are introduced. The accounts of well-known classical experiments are too brief if the reader is to get a real insight into the difficulties which had to be overcome.

For a first edition the book is remarkably free from printer's errors, but others of a more serious nature appear. Until these have been removed the book will tend to be misleading.

On p. 94 the expression $V \cos \theta . t$ is confusing, and somewhat earlier in the text the Greek word *δυναμίς* is spelt *dynamos*. On pp. 159 and 326 a formula is given first with one sign and then with another. The modern tendency is to use a negative sign in expressing the

Newtonian law of gravitation. On p. 219 Poiseuille's formula is quoted and it is not pointed out that the formula given only applies to the flow of an incompressible fluid through a *horizontal* tube.

On p. 310 the term black-body radiation is preferred to full-radiation, and on the next page the formula $W=e\sigma(T_2^4-T_1^4)$ is stated without any suggestion of a proof.

On p. 337 the authors use the term ' normal flux ': surely flux is all that is required, for flux is $\int \vec{A} . \hat{n}\, dS$, where the symbols have their usual meanings.

On p. 367 Ohm's law is given in a form which is not logical. The equation is true numerically and dimensionally, but will be most confusing. Later the importance of using a Weston standard cell at 0° c. is not indicated.

On p. 393 it is stated that Sir J. J. Thomson measured the specific charge of an electron in 1910 : the first experiments were made in 1896 and the results published in 1897. On the following page it is stated that the same apparatus was used for the determination of the charge on a positive ion. This is the most serious error I have noted, for in the first experiments crossed-fields were used while in the second series they were parallel!

On p. 540 a diagram of a Kundt's tube shows (in the gas) a node at the end of the vibrating rod—a fault common to most textbooks.

The treatment of total internal reflection on p. 569 is inadequate and by no means satisfactory. An often-used conventional diagram is given, but the reviewer prefers one in which all the rays emanate from a point source, and, moreover, such diagrams should show that some light is reflected whatever the angle of incidence. The significance of the term " total internal reflection " then becomes more apparent. On p. 617 rays in a spectrometer are shown to have their origin at a point on the surface of a prism, and on the next page a ray suffering minimum deviation does not traverse the prism symmetrically. On p. 648 Newton's rings experiment is shown as Newton did it : it is preferable, however, to place the plate on top of the lens (cf. *Dictionary of Applied Physics*).

The book is well produced and the cost is not excessive, but a less pictorial cover might be more pleasing to many readers. C. J. SMITH.

Applications physiques de la transformation de Laplace, by M. PARODI. Pp. viii + 177. (Centre National de la Recherche Scientifique, 1948.) Price 17*s*. Obtainable from Messrs. H. K. Lewis & Co. Ltd.

In seven chapters, M. Parodi has written a valuable, and distinctly mathematical, survey of his subject. His first chapter is a treatment of the transformation in itself, and is notable for full mathematical rigour, but after this the author rather confuses matters by writing as though the symbolic calculus is identical with the use of the Laplace transformation. Actually, they are quite distinct, though the Laplace transformation provides one way of justifying certain formulae and practices in the other method.

The next three chapters deal respectively with the use of the method in solving ordinary and partial differential equations and in evaluating definite integrals. The fifth chapter applies the method to integral equations, and the sixth, the most advanced and most original, considers the relation between Volterra's *composition* and the Laplace integral. The last chapter is a treatment of electric networks, and steps somewhat outside the limits imposed by the title of the monograph, since it contains an introduction to the general subject of initial admittances and the like. It is thus the most closely related to physical problems.

The C.N.R.S. is doing a very fine work in publishing scientific material in a form somewhat better than we were used to in pre-war French printing. Here the type is clear, the paper good and the lay-out pleasing. The only misleading misprint noted is a y for g in equation (VI.1). J. H. A.

Tables of Scattering Functions for Spherical Particles, by the U.S. NATIONAL APPLIED MATHEMATICS LABORATORIES. Pp. xiii + 119. (Washington : U.S. Department of Commerce, National Bureau of Standards, 1949.) 45 cents.

These tables, prepared under the supervision of Dr. A. N. Lowan in the Computation Laboratory of the National Applied Mathematics Laboratories of the U.S. Bureau of Standards, are derived from the equations given in 1908 by Gustav Mie, which determine rigorously, on classical electromagnetic theory, the diffraction of a plane wave by a sphere of any composition. They are addressed to physicists, chemists, biologists, and others who can use light scattering as a research tool: they originated from work on chemical warfare, and most of them were prepared on the recommendation of V. K. LaMer, professor of chemistry of Columbia University. Professor J. A. Stratton contributes an interesting historical introduction outlining the development of our knowledge of light scattering.

A fundamental parameter in the work is the ratio $(\alpha=)\ 2\pi r/\lambda$ where r denotes the radius of the sphere and λ the wavelength of the incident light. Part I deals with the intensities of the two incoherent plane polarized components scattered by a transparent sphere illuminated with natural light, for α from 0·5 to 6·0; the ratio of the two intensities provides a measure of particle size from 0·05 to 0·2 micron; the angular distribution and total light scattered by a suspension of particles of uniform size can be used to determine their concentration. Angles of scattering at 10° intervals are considered and refractive indices (m) 1·33, 1·44, 1·55, and 2·00.

Part II gives K, the total scattering coefficient (that is, the total energy scattered per second per unit cross-sectional area of particle—illuminated at unit intensity) for $m=5$ and α from 0·5 to 12. Part III deals with the total scattering (and absorbing) coefficient K for absorbing materials (with extinction coefficient k between 0 and 0·1).

Part IV extends the original (LaMer) set of tables to certain complex values of m applicable to the scattering of microwave radar by suspended or falling water drops: these tables use dispersion measurements by J. A. Saxton of the National Physical Laboratory.

As Professor Stratton remarks in his introduction, the great labour expended in preparing this volume will yield ample benefits to physical and biological science, enabling quantitative discussion to replace qualitative ideas. S.C.

Scientific Foundations of Vacuum Technique, by SAUL DUSHMAN. Pp. xi+882. 1st Edition. (New York: John Wiley; London: Chapman & Hall, 1949.) 90*s*.

The introduction of Gaede's mercury diffusion pump marked the commencement of great advances in high-vacuum technique. A new industry—vacuum technology—has grown up, and a small-scale laboratory operation has been transformed within the past forty years into an industrial one, carried out on a scale that would have been almost inconceivable in the minds of the early workers in the field. Speed, and greater speed, is demanded for the exhaustion of all types of electronic equipment, cyclotrons, betatrons, etc., and for vacuum distillation, dehydration and the evaporation of metals and other substances. These higher speeds have been attained by paying more attention to jet design in pumps.

Only a few books have been written on the subject, and the first one to appear was that written by Dr. Dushman in 1922. The recent rapid advances have more than justified the present volume, which workers in this field have required for some time. In spite of its 882 pages, and of the fact that it contains a reference to the researches of practically every investigator in high-vacuum technique, it is no mere encyclopaedia, no catalogue of methods and results, but contains the theory which is so essential if successful operations are to be understood and appreciated. It is not only a complete revision of the earlier work, but it includes a very considerable amount of new material. The diagrams are numerous and good, and a useful feature is the copious references to original papers.

The opening chapters deal with the kinetic theory of gases and their flow through tubes and orifices, features which play important parts in high-vacuum work and which considerably affect pumping speeds. The treatment of mechanical and vapour pumps is interesting and explicit. The rôles of diffusion and condensation are discussed, and the extreme importance of jet design is fully explained. Alexander's modern type of pump is described and reasons are given why all vapour pumps do not function as diffusion ones—a conclusion which agrees with Langmuir's view on their operation. Manometers receive full treatment and the various indispensable leak detectors are included. Then follows a description of other methods whereby gases may be removed from vessels, such as the sorption of gases and vapours by solids, and in particular by activated charcoal, silicates, cellulose and metals. Diffusion through the latter and degassing problems are also fully discussed. The chapter on chemical and electrical clean-up of gases at low pressures gives a comprehensive survey of the clean-up of gases by evaporated metals, technical getters, incandescent filaments, cold and hot cathode discharges, and the production of extremely low pressures in sealed-off devices. The later chapters deal with vapour pressures, rates of evaporation and dissociation pressures—including useful information on vacuum distillation—and the deposition of films.

The book is a complete treatment of the subject, one which should be in the hands of every worker in the fields of physics, engineering and chemistry.

F. H. NEWMAN.

An Introduction to Color, by R. M. EVANS. Pp. x + 340. 1st Edition. (New York: J. Wiley & Sons; British Agents: Chapman & Hall, London, 1948.) 36*s*.

This is a book which should be read by every physicist who is interested in colour. So far as the purely physical aspects are concerned, he may find himself fairly familiar with those chapters dealing with light, light sources, illumination, spectral reflection and absorption, etc., although he will find these subjects dealt with in an instructive and lucid manner. He may be surprised at the complete absence of any algebra, yet he will discover most of the essential mathematics is present in the, to many people, more palatable form of graphs and diagrams. The outstanding virtue of the book, however, is in its breadth rather than its depth. Rarely, if ever before, has a book been written on colour in which the physics, physiology, psychology, aesthetics and technology of colour have been treated in such a balanced and sane manner. There is no suggestion that one approach is more correct or more important than another ; on the contrary, the reader is left with a very clear impression of the inter-relation and inter-dependence of all these aspects. The physicist may even find it a humbling experience to read the book, because he can hardly fail to recognize that the physical aspect is the least subtle and least fascinating of any. He will, in particular, be introduced to many psychological factors which he had hitherto tended to ignore and to problems of perception of whose existence he was probably unaware.

Apart from its value to himself, the physicist will welcome this book as one which he can confidently recommend to his more artistically minded friends, and in particular to the art master at school. The physicist has a legitimate grievance that right from his earliest years the youngster at school learns about colour in a manner that is scientifically misleading. A boy discovers that when he mixes yellow and blue paints, he produces green, but he is quite unaware whether this result is due to the light or the pigment or the eye. From this initial half-conception comes much of the subsequent misunderstanding between the scientist on the one hand and the artist and craftsman on the other. We can recognize that it is not going to be easy to explain about spectral absorption to the boy or girl in his primary school, but we can at least expect the teacher himself to have some understanding of the problem. Evans' *Color* will give him most of what he needs to know in a manner which canot fail to delight him.

This is undoubtedly a very fine book, refreshingly modern, beautifully produced and profusely illustrated. There are, no doubt, some details and omissions which might be criticized, but it would be churlish to dwell on these. We should, on the contrary, congratulate the author on a very fine achievement and hope for a wide and increasing circulation for his book.

W. D. WRIGHT.

Foundations of Modern Physics, by T. B. BROWN. Pp. xvi + 391. 2nd Edition. (New York: John Wiley & Sons; British Agents: Chapman & Hall, 1949.) 30*s*.

Professor Brown's book is successful if its aim is to give to science students, in their last year at school or in their first year at the university, a sketch of the type of experiments and an outline of the ideas which form the basis of modern physics.

The production of the present work is excellent, the printing is good, the diagrams are clear and concentrate on fundamentals, and there are extremely few errors of any kind. There does not seem to be any way in which the treatment of so wide a subject could be substantially improved within the limits of 400 pages. Yet it does not seem possible to deny that the analysis is shallow ; also the contribution of American workers is over-emphasized in the last few chapters. Perhaps the author can hardly be blamed for this since the advance of modern physics has been so rapid and on so wide a front that some selection is inevitable. Indeed, the reviewer feels that the days when a semi-popular exposition of physics can be undertaken are rapidly drawing to a close. No one expects advances in modern mathematics to be made generally intelligible or available to first-year students, and certainly the number and quality of those engaged in advancing modern physics is such that the breadth, content and complexity of the subject are likely to increase still further.

F. C. CHAMPION.

Corrigenda

" Wave-front Aberrations of Oblique Pencils in a Symmetrical Optical System: Refraction and Transfer Formulae ", by W. WEINSTEIN (*Proc. Phys. Soc.* B, 1949, **62,** 726).

Page 733, equation (14), the first term in the bracket on the right-hand side *should read*

$$\tfrac{3}{2}\sin I\cos I\left(\frac{\cos I}{r}-\frac{2\cos^2 I}{t}\right)C_{30}$$

instead of

$$\tfrac{3}{2}\sin I\cos I\left(\frac{\cos I}{r}-\frac{\cos^2 I}{t}\right)C_{30}.$$

Page 737, equation (29), the left-hand side of the equation *should read*

$$\Delta(C_{22}N\cos^2 I) \quad \textit{instead of} \quad \Delta(C_{12}N\cos^2 I).$$

On the right-hand side, the first term in the second line *should read*

$$+\frac{3}{2r}C_{30}\sin I\cos^2 I \quad \textit{instead of} \quad -\frac{3}{2r}C_{30}\sin I\cos^2 I,$$

and the first term in the third line *should read*

$$+\frac{1}{4r^3}\cos I \quad \textit{instead of} \quad +\frac{1}{8r^3}\cos I.$$

Reprints of Papers in the 'Proceedings of the Physical Society'

In general, reprints of papers published in the *Proceedings of the Physical Society* are not available at the Offices of the Society, but may occasionally be obtained from the authors of the papers concerned. The address of the author is given at the head of each paper.

Exceptions to this are the special Lectures delivered before the Society, such as the Guthrie Lecture, the Presidential Address, the Charles Chree Lecture and the Rutherford Lecture.

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ABSTRACTS FOR SECTION A

The Band Spectrum of GeF, by E. B. Andrews and R. F. Barrow.

ABSTRACT. Two band-systems attributed to GeF have been observed in emission from a discharge through a stream of GeF_4 vapour. Vibrational analyses of both systems have been made and the following constants derived :

State	ν_e	ω_e	$x_e\omega_e$ (cm^{-1})
? $^2\Sigma$	35007·4	800·4	$4{\cdot}1_5$
? $^2\Sigma$	23316·8	413·5	$1{\cdot}0_5$
$^2\Pi_{3/2}$	935	665·8	$2{\cdot}8_3$
$^2\Pi_{1/2}$	0	664·5	$2{\cdot}7_4$

A brief discussion of the results, and a comparison between the force-constants of the mono- and tetra-halides of the group IV–B elements, is given.

On the Interactions of Dislocations and Solute Atoms, by B. A. Bilby.

ABSTRACT. An extension of the reciprocal theorem of Colonetti is given and with it a general expression derived for the elastic energy of a multiply-connected solid containing sources of internal stress and subjected to external forces. The terms in the energy which depend on the relative position of a selected source of stress with respect to the field of all the others can be separated. The expression is used to estimate approximately the interaction energy between parallel edge dislocations with arbitrary slip vectors, between parallel screw dislocations and between an edge dislocation and a solute atom causing a spherical distortion of the lattice.

Spin-Lattice Relaxation in some Paramagnetic Salts, by R. J. Benzie and A. H. Cooke.

ABSTRACT. The magnetization of a paramagnetic salt is a relaxation process with a relaxation time depending on the external field and temperature. Measurements have been made with the object of determining relaxation times at various fields and temperatures in the liquid helium range. A description of the apparatus is given.

The results show that paramagnetic relaxation is a complex phenomenon, and suggest that in any one specimen it must be described in terms of a distribution of relaxation times rather than a single relaxation time. In general we find that relaxation times are of the order of 10^{-2} sec., with a temperature dependence according to a power of $1/T$ between 2 and 3, while increasing with the external field H according to a power of H between 0 and 1.

Specific Heats of some Paramagnetic Salts at Temperatures near 1° K., by R. J. Benzie and A. H. Cooke.

ABSTRACT. The magnetic specific heats of gadolinium sulphate and of several salts of the iron group of transition elements have been measured at temperatures near 1° K. by a method depending on paramagnetic relaxation. The results obtained are analysed into contributions due to magnetic dipole coupling and interaction of the magnetic ions with the electric field of the crystalline lattice. Cases in which these contributions are insufficient to account for the observed specific heats are discussed.

The 'External' Photoelectron Spectrum and the Intensities of the γ-Rays of Thorium $(B+C+C'')$, by D. G. E. Martin and H. O. W. Richardson.

ABSTRACT. The spectra of the photoelectrons ejected from various targets by the γ-rays of $\mathrm{Th}(\mathrm{B}+\mathrm{C}+\mathrm{C}'')$ have been measured and the emission probabilities of the γ-rays of energy 0·238, 0·277, 0·299, 0·510, 0·582, 0·726, and 0·859 Mev. have been estimated. Using the known intensities of the internal conversion lines, coefficients of internal conversion have been found. The four low-energy rays seem to be magnetic dipole in character with some electric quadripole admixture, but the strong 0·582 Mev. ray of $^{208}\mathrm{Pb}$ is predominantly electric quadripole. The possible spins of the nuclear levels are discussed.

Ellis and Aston's Theory of the Height of a Photoelectron Line, by H. O. W. Richardson.

ABSTRACT. The formula of Ellis and Aston relating the intensity of a γ-ray to the height of its photoelectron line produced from a thick target is revised using the quantum-mechanical theory of stopping power. The effects of multiple scattering, bremsstrahlung and anistropic emission of the photoelectrons are discussed and a general comparison of thick and thin target methods is made.

Note on the Fluctuation Problem of Cascades, by L. Jánossy.

ABSTRACT. Diffusion equations governing the fluctuations of nucleon cascades and also of electron–photon cascades are given. The electron cascade is treated at first in the usual approximation, but it is shown that the approximations are not essential for the treatment. The diffusion equations appear in the form of integro-differential equations which can be solved directly using numerical integration. It is hoped to present numerical solutions in a later publication.

Some Observations on the Nuclear Disintegrations caused by Cosmic Rays in Photographic Emulsions, by Nora Page.

ABSTRACT. An account is given of a study of 2,150 stars in Ilford C2 plates and 312 stars in Kodak NT4 plates exposed under different conditions. Possible values for the cross section for star-producing collisions are discussed. It is concluded that this collision cross section is equal to the geometrical cross section of the nuclei, and that the star-producing particles are non-catastrophically absorbed, leading to the observed absorption cross sections. It is shown that nuclear transparency could not account for the observed results. It is estimated that 17% of all stars and 40% of stars from which two or more lightly ionizing particles are emitted are caused by ionizing primary particles. The size distributions for stars caused by ionizing and non-ionizing particles are given, and possible explanations for the difference between them are considered. The experimental observations are in agreement with the theory that the star-producing particles are mainly neutrons and protons secondary to the primary cosmic rays.

The variation with star size of the proportion of doubly charged to singly charged particles is found, and for stars of more than six prongs is in agreement with Le Couteur's extension of the evaporation theory. A value of 0·54 is deduced for the proportion of doubly charged particles from disintegrations in the light elements of the emulsion.

An increase in the proportion of lightly ionizing tracks is observed for stars of more than eight prongs, and is ascribed to the creation of mesons.

The Evaporation Theory of Nuclear Disintegrations, by K. J. Le Couteur.

ABSTRACT. The relationship between nuclear temperature and excitation energy is discussed taking into account the thermal expansion of the nucleus and the effect of the neutron excess. Using these results, the evaporation theory is put into a form suitable for the treatment of highly excited nuclei. The competition between the emission of proton, neutron, deuteron, triton and α-particle is considered in detail, using Weisskopf's method of detailed balance.

Detailed numerical values are calculated for the disintegrations of silver bromine observed in photographic plates. The main points of comparison with experiment are (i) the energy distribution of the evaporated particles, and (ii) the ratio of emission of singly and doubly charged particles. The comparison yields close information about the relationship of nuclear energy and temperature; the agreement with theory is as good as can be expected. It is necessary to assume that the Coulomb potential barrier is reduced at high excitation energies.

The Correction of Specific β-Radioactivity for Self-Absorption by C. H. Collie, P. F. D. Shaw and H. J. Gale.

ABSTRACT. The self-absorption of β-rays in radioactive films between 5 and 100 mg/cm^2 superficial density has been investigated. The marked departures from the exponential absorption law are shown to be due to scattering of the β-rays in the film. The use of very thin films to avoid the correction for self-absorption is not recommended as a routine method.

The Magneto-Resistance of the Alkali Metals, by D. K. C. MacDonald.

ABSTRACT. The magneto-resistive effect has been examined experimentally in the alkali metals at low temperatures. It is concluded that deviations from the free electron gas model become considerable in the case of the heavier metals, caesium and rubidium.